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CATHODIC REDUCTION OF METAL-CHLORIDE COORDINATION IONS①

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ABSTRACT

The reduction mechanism of metal chloride coordination ions is elucidated with elemental and experimental study. Through the elemental study one can know that the galvanostatic step method or chronopotential curves are very convenient to the determination of cathodic reduction mechanism of metal chlorides. Through the variation of $i\tau^{1/2}$ with the concentration of Cl^- the discharging species at the surface of cathode can be determined as well as the reaction mechanism, cuprous chloride, zinc chloride and lead chloride are used as examples to illustrate the elemental study. Their reaction mechanism can be expressed as:

(1) $CuCl_3^{2-} \leftrightarrows CuCl_2^- + Cl^-$ is a fast preceding reaction, and $CuCl_2^- + e \rightarrow Cu + 2Cl^-$ is a discharging reaction with mass transfer determined step.

(2) $ZnCl_3^- \leftrightarrows ZnCl_2 + Cl^-$ is a fast preceding reaction, and $ZnCl_2 + 2e \rightarrow Zn + 2Cl^-$, one step discharging with diffusion controlling step.

(3) $PbCl_4^{2-} + 2e \rightarrow Pb + 4Cl^-$ and $PbCl_3^- + 2e \rightarrow Pb + 3Cl^-$, there is no preceding reaction involved in the lead chloride case and the direct discharging step is also controlled by the diffusion step.

Key words: cathodic reduction metal chloride coordination ions copper chloride zinc chloride lead chloride chronopotential method

1 INTRODUCTION

Chlorinate hydrometallurgy is a special good technology for extracting metals from various complex and low grade minerals. Metals can be obtained by electrowinning from purified chloride solutions.

Aqueous solutions of chlorides are usually of good conductivity and high current efficiency, therefore low energy consumptions in electrowinnings or electrolyses can be expected.

As for the determination of reaction mechanism in electrode processes, there are still more difficulties. The first obstacle is what species in variety of coordination chlorides can directly discharge at the electrode. Even the determination of electrochemical reaction order is helpful but with some limit[1].

This paper elucidates the reduction mechanism of metal-chlorides by galvanos-

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tatic step method. The equations for the determination of electrode mechanism will be given in the paper and the experimental examples for the use of the elemental study will also be reported in the paper.

2 ELEMENTAL STUDY

2. 1 *Model for Electrode Reactions*

Many of metallic ions in chloride solutions are coordination ions. Those with high or higher coordination mumber are rather stable in energy but difficult to reduce directly at the electrode. The species reduced directly at the electrode are usually those coordination ions with low coordination number, which may be considered as a general rule. Let $MCl^{(n-\mu)+}$, or MCl_μ be a stable species, and $MCl_\delta^{(n-\delta)+}$, or MCl_δ, be a direct reduced species at the electrode. The reduction reaction can be represented by:

$$MCl_\mu \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MCl_\delta + (\mu - \delta)Cl^- \qquad (1)$$

$$MCl_\delta + ne \rightarrow M + \delta MCl^- \qquad (2)$$

The dissociate reaction (1) is the reaction preceding charge transfer where $\mu > \delta$.

2. 2 *Expressions for Concentration of* MCl_δ *at Electrode Surface*, $C_{MCl}(0, t)$, *and Transition Time* τ

The dissociate constant K for reaction (1) is:

$$K = \frac{k_1}{k_{-1}} = C_{MCl_\delta} \cdot C_{Cl}^{\mu-\delta} / C_{MCl_\mu} \qquad (3)$$

Let $k_a = k_1 \qquad (4)$

$$k_b = k_{-1} C_{Cl}^{\mu-\delta} \qquad (5)$$

$$C^0 = C_{MCl_\mu} + C_{MCl_\delta} \qquad (6)$$

Its concentration and distribution of direct discharge species MCl_δ with the distance (x) from the electrode and with reaction time (t) are represented by $C_{MCl_\delta}(x, t)$ and by $C_{MCl_\delta}(0, t)$ at the surface of electrode. $C_{MCl_\delta}(0, t)$ can be solved by Laplace transform for the active diffusion equation under conditions of galvanostatic steps[2], and the concentration of coordination ions far larger than the concentration of metallic ions, thus the concentration of MCl_δ at the surface of electrode can be expressed as:

$$MCl_\delta(0, t) = \frac{K}{C_{Cl}^{\mu-\delta} + K}\{C^0 - \frac{2i_k t^{1/2}}{nF\pi^{1/2}D^{1/2}} - \frac{i_k C_{Cl}^{\mu-\delta}}{nFD^{1/2}K(k_a + k_b)^{1/2}} \times \operatorname{erf}(k_a + k_b)^{1/2} t^{1/2}\} \qquad (7)$$

where i_k is current density under galvanostatic condition, D is diffusion coefficient, t is reaction time, erf( ) is error function, and others are conventional signs. While $C_{MCl_\delta}(0, t) = 0$, then the transition time, τ, can be obtained from equation (7):

$$i_k \tau^{1/2} = \frac{nF\pi^{1/2}D^{1/2}C^0}{2} - \frac{i_k \pi^{1/2} C_{Cl}^{\mu-\delta}}{2K(k_a + k_b)^{1/2}} \times \operatorname{erf}[(k_a + k_b)^{1/2} \tau^{1/2}] \qquad (8)$$

2. 3 *Determination of Mechanism of Electrode Reaction*

For an electrode process with fast preceding reaction, i. e. $i_k \ll \frac{2K(k_a + k_b)^{1/2}}{\pi^{1/2} C_{Cl}^{\mu-\delta}}$, the second term can be ignored, then

$$i_k \tau^{1/2} = \frac{nF\pi^{1/2}D^{1/2}C^0}{2} \qquad (9)$$

Equation (9) shows that $i\tau^{1/2}$ is independent on i_k and proportional to C^0. Put equations (3) and (6) into (9), then a logarithmic equation can be obtained:

$$\lg(\frac{2i_k \tau^{1/2}}{nF\pi^{1/2}D^{1/2}C_{MCl_\mu}} - 1) = \lg K - (\mu - \delta)\lg C_{Cl^-} \qquad (10)$$

If the velocities of preceding reaction and the discharge reaction are not much different and i_k is small, then $(k_a + k_b)^{1/2}\tau^{1/2} > 2$, and $\operatorname{erf}[(k_a + k_b)^{1/2}\tau^{1/2}] \approx 1$, therefore equation (8) can be simplified as:

$$i_k\tau^{1/2} = \frac{nF\pi^{1/2}D^{1/2}C^0}{2} - \frac{\pi^{1/2}C_{Cl}^{\mu-\delta}}{2K(k_a + k_b)^{1/2}}i_k \qquad (11)$$

It means that $i_k\tau^{1/2}$ is a linear function of i_k. If $i_k \to 0$, then

$$(i_k\tau^{1/2})_{i_k\to 0} = \frac{nF\pi^{1/2}D^{1/2}C^0}{2} \qquad (12)$$

Let $$B = \frac{\pi^{1/2}C_{Cl}^{\mu-\delta}}{2K(k_a + k_b)^{1/2}} \qquad (13)$$

follow the example of equation (10) obtained from equation (9), equation (14) can be obtained:

$$\lg\left[\frac{2(i_k\tau^{1/2})_{i_k\to 0}}{nF\pi^{1/2}D^{1/2}C_{MCl^-}} - 1\right] = \lg K - (\mu - \delta)\lg C_{Cl^-} \qquad (14)$$

Making logarithm of equation (13) and put equations (4) and (5) into it, and considering $K << 1$, then $k_{-1} >> k_1$, one can get:

$$\lg B = \lg\frac{\pi^{1/2}}{2Kk_{-1}^{1/2}} + \frac{1}{2}(\mu - \delta)\lg C_{Cl^-} \qquad (15)$$

If $K >> 1$, then $k_{-1} << k_1$, and equation (16) obtained instead of equation (15):

$$\lg B = \lg\frac{\pi^{1/2}}{2Kk_1^{1/2}} + (\mu - \delta)\lg C_{Cl^-} \qquad (16)$$

For those with slow preceding transfer reaction and large i_k, $[(k_a + k_b)\tau^{1/2}] < 0.1$ is valid, and the error function erf $[(k_a + k_b)^{1/2}\tau^{1/2}]$ can be simply expressed by the first term of its series, then equation (8) can be simplified as equation (17):

$$i_k\tau^{1/2} = \frac{nF\pi^{1/2}D^{1/2}C^0}{2}\left(1 + \frac{C_{Cl}^{\mu-\delta}}{K}\right) \qquad (17)$$

Put equations (3) and (6) into equation (17), then:

$$i_k\tau^{1/2} = nF\pi^{1/2}D^{1/2}C_{MCl_\delta}/2 \qquad (18)$$

From equation (18) it can be seen that $i_k\tau^{1/2}$ is independent on i_k but proportional to the concentration of MCl_δ, which is the species of reducing directly at the surface of electrode.

Put equation (3) into equation (18), then:

$$\lg\left(\frac{2i_k\tau^{1/2}}{nF\pi^{1/2}D^{1/2}C_{MCl_\mu}}\right) = \lg K - (\mu - \delta)\lg C_{Cl^-} \qquad (19)$$

From equations (10), (14) and (19) one can see that by the measurement of the variation of $i_k\tau^{1/2}$ with C_{Cl^-} and the concentration of MCl_μ, which is the main species of coordination compounds, is given, the species, MCl_δ, reducing directly at the surface of the electrode can be determined and the electrode mechanism as well.

2.4 *Equations for Chronopotential Curves*

In both very fast and very slow speeds of the preceding transfer reaction, as equations (9) and (18) show that $i_k\tau^{1/2}$ is independent on i_k, which is the feature of simple charge transfer and proportional to $C_{MCl_\mu} + C_{MCl_\delta}$ for the fast one, and to C_{MCl_δ} for the slow one.

Under the condition of $i_k << \frac{2K(k_a + k_b)^{1/2}}{\pi^{1/2}C_{Cl}^{\mu-\delta}}$ and put equations (3), (6) and (9) into equation (7), or under the condition $(k_a + k_b)^{1/2}\tau^{1/2} < 0.1$, i. e. $(k_a + k_b)^{1/2}t^{1/2} < 0.1$ and put equations (3), (6) and (18) into equation (7), the concentration of the direct discharge species MCl_δ at the surface of electrode can be expressed by the transition time τ:

$$C_{MCl_\delta}(0,t) = C_{MCl_\delta}\tau^{1/2} - t^{1/2}/\tau^{1/2} \qquad (20)$$

For a reversible process with insoluble product, put equation (20) into Nernst equation:

$$\varphi_t = \varphi_{r(MCl_\delta/M)} + \frac{RT}{nF}\ln\frac{\tau^{1/2} - t^{1/2}}{\tau^{1/2}} \qquad (21)$$

For an irreversible process, put equation (20) into Butler-Volmer equation:

$$\varphi_t = (\varphi_{rMCl_\delta/M}) + \frac{RT}{\alpha nF}\ln\frac{i_0}{i_k} +$$

$$\frac{RT}{\alpha nF}\ln\frac{\tau^{1/2}-t^{1/2}}{\tau^{1/2}} \qquad (22)$$

In the case of reactions with the same order of discharge velocity and preceding transfer velocity, e. g. $(k_a+k_b)^{1/2}\tau^{1/2}>2$, $(k_a+k_b)^{1/2}t^{1/2}>2$ and $\mathrm{erf}[(k_a+k_b)^{1/2}t^{1/2}]\approx 1$, put equations (3), (6), (11) and (13) into equation(7), the concentration of MCl_δ at the surface of electrode can be expressed by τ:

$$C_{MCl_\delta}(0,t)=C_{MCl_\delta}\frac{\tau^{1/2}-t^{1/2}}{\tau^{1/2}+B} \qquad (23)$$

For a reversible process with insoluble product, put equation(23) into Nernst equation:

$$\varphi_t=\varphi_{r(MCl_\delta/M)}+\frac{RT}{\alpha nF}\lg\frac{\tau^{1/2}-t^{1/2}}{\tau^{1/2}+B} \qquad (24)$$

For an irreversible process, put equetion (23) into Butler-Volmer equation:

$$\varphi_t=\varphi_{r(MCl_\delta/M)}+\frac{RT}{nF}\ln\frac{i_0}{i_k}+\frac{RT}{\alpha nF}\ln\frac{\tau^{1/2}-t^{1/2}}{\tau^{1/2}+B} \qquad (25)$$

From the derivation above we can see that the cathodic reduction of metallic coordination ions and their kinetic parameters can be obtained by measuring chronopotential curves.

3 EXPERIMENTAL STUDY

3.1 *Experimental Equipment and Chemicals*

The electrochemical measurement system was composed of the standard direct current resources type YZAV-1 and the function recorder type LZ-—204. A H type electrolytic cell with a large P_t auxiliary electrode and a working electrode was used in the measurement. The working electrodes were high purity copper (99.99%), lead and zinc with an area of 0.006 cm^2 and polished to mirror smooth. All solutions for the experiments were made from analytical reagents and twice distilled water. Nitrogen was used to remove oxygen in the solution, the electro-chemical measurements were started after the deoxygen about 15～20 min in order to still the solution. The temperature was kept at 30 + 0.02 ℃ by a super thermostat type DL-501. A saturated calomel electrode was used as reference electrode, and a Luggin capillary tube and a salt bridge were also put between the working electrode and reference electrode.

3.2 *Results*

The coordination ions of Cu(Ⅰ), Pb(Ⅱ) and Zn(Ⅱ) were reduced with only one wave on the chronopotential curves, as shown in Fig. 1, and the transition time τ decreases with the increase of current density i_k. The plot of $i_k\tau^{1/2}$ against i_k is shown in Fig. 2, in which horizontal lines indicate that $i^k\tau^{1/2}$ is independent on i_k.

The linear relations of φ_t (electrode potential at time t) with $\lg\frac{\tau^{1/2}-t^{1/2}}{\tau^{1/2}}$ were obtained from the mathematic treatment of data on the basis of chronopotential curves of Fig. 1 and the plot is shown in Fig. 2. The slopes for Cu(Ⅰ), Pb(Ⅱ) and Zn(Ⅱ) are 0.031, 0.60 and 0.059 V respectively, the intersection values are independent on the current densities i_k.

The electron number n of reduction for Cu(Ⅰ), Pb(Ⅱ) and Zn(Ⅱ) can be obtained from the slopes in Fig. 3, and they are 1, 2 and 2 respectively.

The reductions of Cu(Ⅰ), Pb(Ⅱ)and Zn(Ⅱ) in chloride solution are with the feature of simple charge transfer or the fast preceding transfer reaction and with the feature of reversible electrode process, as indicated by equation (20).

3.3 *Discussion*

It is indicated by experimental data and theoretical calculations that Cu (Ⅰ), Pb (Ⅱ) and Zn (Ⅱ) ions in chloride solution exist as different coordination ions. According to equilibrium calculations of coordination[3,4], in chloride solution of 2～5 mol · L^{-1} the main species of coordination for Cu (Ⅰ) is $CuCl_3^{2-}$, for Pb(Ⅱ) is $PbCl_4^{2-}$ and $PbCl_3^-$, and for Zn(Ⅱ) is $ZnCl_3^-$. The ratio of main species increases with the increase of the chloride concentration. For example 92.7% of Cu(Ⅰ) exists as $CuCl_3^-$, 87.1% of Zn(Ⅱ) exists as $ZnCl_3^-$, 43.2% and 50.3% of Pb(Ⅱ) exist as $PbCl_4^{2-}$ and $PbCl_3^-$ respectively as the concentration of Cl^- increases to 3.5 mol · L^{-1}.

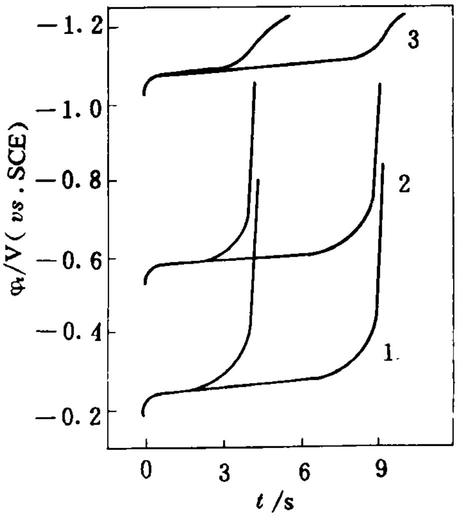

Fig. 1 **Chronopotential curves**(30 ℃)
1—12.5, 8.4 $Cu_2Cl_2$0.01+HCl0.1+NaCl3.4
2—25.0, 16.8 $PbCl_2$0.01+HCl0.1+NaCl3.4
3—25.0, 16.8 $ZnCl_2$0.01+NaCl3.5

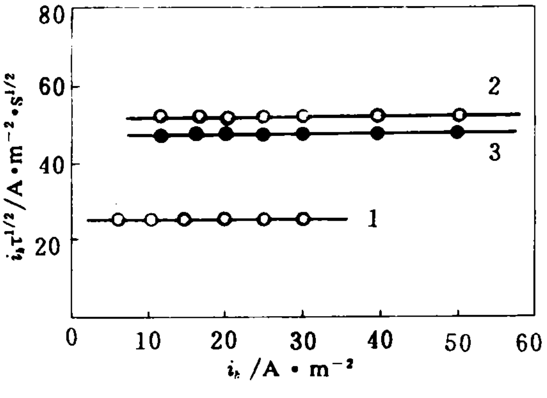

Fig. 2 **Plot of $i_t\tau^{1/2}$- i_t (30 ℃) under the same solution as in Fig. 1**

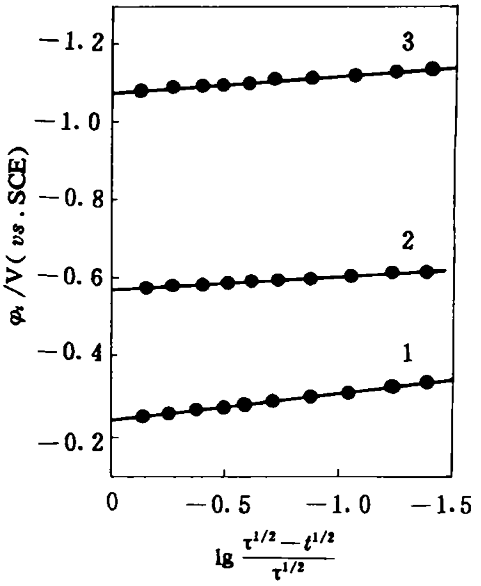

Fig. 3 **Plot of φ_t-lg $\frac{\tau^{1/2}-t^{1/2}}{\tau^{1/2}}$**
Under the same condition as in Fig. 1

Therefore the overall reactions for the reductions of Cu(Ⅰ), Pb(Ⅱ) and Zn(Ⅱ) can be expressed as:

$$CuCl_3^{2-} + e \rightarrow Cu + 3Cl^-$$

$$PbCl^{(x-2)}{)}_x + 2e \rightarrow Pb + xCl^-$$

where x is 3 and 4

$$\text{and } ZnCl_3^- + 2e \rightarrow Zn + 3Cl^-$$

If the main species are expressed by $MCl_\mu^{(n-\mu)+}$ or MCl_μ, then the preceding transfer reaction can be represented by:

$$MCl_\mu^{(n-\mu)+} \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} MCl_\delta + (\mu-\delta)Cl^-$$

$$\text{or } MCl_\mu \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} MCl_\delta + (\mu-\delta)Cl^-$$

Thus the reductions of Cu (Ⅰ), Pb (Ⅱ) and Zn (Ⅱ) in chloride solution followed the model of reversible electrode process and fast preceding transfer reaction, it is to say, equation(10),

$$\lg\left(\frac{2i_k\tau^{1/2}}{nF\pi^{1/2}D^{1/2}C_{\mathrm{MCl}_\mu}}-1\right)$$
$$=\lg K-(\mu-\delta)\lg C_{\mathrm{Cl}^-}$$

can be used for these reactions. Let $f(\tau)=\lg\left(\frac{2i_k\tau^{1/2}}{nF\pi^{1/2}D^{1/2}C_{\mathrm{MCl}}}-1\right)$ where i_k, τ, C and n are determined in this study, D the diffusion coefficert is either determined by our experiment[5] or gotten from literature. A plot of $f(\tau)$ against $\lg C_{\mathrm{Cl}^-}$ is shown in Fig. 4. The value $-(\mu-\delta)$ can be determined by the slopes of straight lines in Fig. 4. They are −0.85, −0.95 and 0 for CuCl_3^-, ZnCl_3^- and $\mathrm{PbCl}_x^{(x-2)-}$ respectively. That is to say, $\mu-\delta\approx 1$ for Cu(Ⅰ) and Zn(Ⅱ), and $\mu-\delta=0$ for Pb(Ⅱ). Thus, the fast preceding transfer reactions for Cu(Ⅰ) and Zn(Ⅱ) are: one ligand Cl^- dissociated from the main species and turned to be the CuCl_2^- and ZnCl_2 coordination species, by which the discharge at the surface of electrode would happen more easily. For the Pb(Ⅱ) case, probably there is no preceding transfer reaction and the PbCl_4^{2-} or PbCl_3^- directly discharged at the surface of electrode.

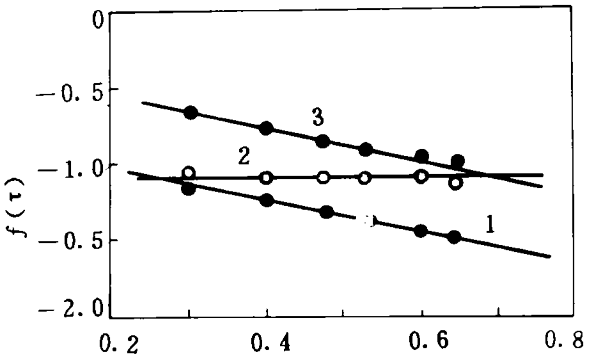

Fig. 4 plot of $f(\tau)$ against $\lg C_{\mathrm{Cl}}$
(Concentrations are in mol·L^{-1})

1—0.01**CuCl**+0.1**HCl**+ x **NaCl**+(4.5− x)**NaClO$_4$**; 2—0.01**PbCl$_2$** + 0.1**HCl$_x$ NaCl** + (4.5 − x)**NaClO$_4$**; 3—0.01**ZnCl$_2$** + x **NaCl** + (4.6 − x)**NaClO$_4$**

4 CONCLUSIONS

(1) By the measurement of the relation of transition time τ with the concentration of Cl^- the species that directly discharge at the surface of electrode can be determined.

(2) The reduction of Cu(Ⅰ) and Zn(Ⅱ) in chloride solution subject a fast preceding transfer reaction prior to discharge, and their electrode processes follow the model of mass transfer controlling. Their discharge of one step involves one electron for Cu(Ⅰ) and two electrons for Pb(Ⅱ) and Zn(Ⅱ). Their electrode reactions can be expressed by following equations:

$$\mathrm{CuCl}_3^{2-}\rightarrow\mathrm{CuCl}_2^-+\mathrm{Cl}^-$$
$$\mathrm{CuCl}_2^-+e\rightarrow\mathrm{Cu}+2\mathrm{Cl}^-$$
$$\mathrm{PbCl}_4^{2-}+2e\rightarrow\mathrm{Pb}+4\mathrm{Cl}^-$$
$$\mathrm{PbCl}_3^-+2e\rightarrow\mathrm{Pb}+3\mathrm{Cl}^-$$
$$\mathrm{ZnCl}_3^-\leftrightarrows\mathrm{ZnCl}_{2(aq)}+\mathrm{Cl}^-$$

and $$\mathrm{ZnCl}_{2(aq)}+2e\rightarrow\mathrm{Zn}+2\mathrm{Cl}^-$$

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