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ELECTROREDUCTION OF Zn^{2+} AND Ni^{2+} AND Cu^{2+} IN UREA-CHLORIDES MELT①

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ABSTRACT The cyclic voltammetry, current-time curve at potential step were used to investigate the electroreduction of Zn^{2+}, Ni^{2+} and Cu^{2+} in the urea-chlorides melt. Experimental results indicate that the electoreduction of Zn^{2+} to zinc is reversible in one step, the electoreduction of Ni^{2+} to nickel is irreversible in one step and the electroreduction of Cu^{2+} to copper is reversible with two steps. The diffusion coefficients of Zn^{2+}, Ni^{2+} and Cu^{2+} in urea-chlorides melt and the transfer coefficient of $Ni^{2+} + 2e \rightarrow Ni$ were determined.

Key words urea-chlorides melt electroreduction of Zn^{2+}, Ni^{2+} and Cu^{2+} diffusion coefficient transfer coefficient

1 INTRODUCTION

Many metal chlorides are easily soluble in the urea melt. The electric conductivities of urea-metal chlorides at 125 ℃ can attain to 3 S·m^{-1}[1]. Sarnavskii obtained the strongly adhering plate of nickel on titanium, stainless steel substrates (on which other metals do not adhere) by electroplating in urea-$NiCl_2$-Na benzoate melt[2]. The Zn-Ti, rare earth-ferrous alloys (for example the La-Co electrodeposit in urea melt) were obtained by us[3]. Therefore, the technological application for the electrodeposition of metals and their alloys in urea melt is promising. The research for the electroreduction of the metallic ion in urea melt is very deficient. In this paper, the electrode processes for the reduction of Zn^{2+}, Ni^{2+} and Cu^{2+} in urea-metal chlorides were investigated and some kinetic parameters were determined.

2 EXPERIMENTAL

Urea, NaCl, $ZnCl_2$, $NiCl_2\cdot 6H_2O$ and $CuCl_2\cdot 2H_2O$ were analytical pure. The hydrous salts and the moist $ZnCl_2$ were dehydrated in vacuum at 120 ℃. All compounds used here were storaged in the desiccator contained P_2O_5.

The working electrodes were spectral pure graphite, titanium and copper. The counter electrode was spectral pure graphite. The reference electrode was Ag / urea − NaCl (6.0% (in weight)). The mixture of urea and salts in the glass cell was melted at the temperature lower than 130 ℃. Cyclic voltammogram (CV) and current-time curve at potential step were made with DCD− 3 functional generator, HDV− 7B potentiostat, and 3086 X-Y recorder. Electrochemical measurements were proceeded under argon atmosphere. The temperature was controlled with oil-bath thermostat.

3 RESULTS AND DISCUSSION

3.1 *Electroreduction of* Zn^{2+}

3.1.1 Voltammogram

The cyclic Voltammogram of graphite electrode in urea-NaCl-$ZnCl_2$ at 125 ℃ is shown in Fig. 1. Two cathodic waves started at − 1.06 V and − 1.27 V, respectively. The starting potential of the 2nd cathodic wave was very close to the cathodic limit of the urea-NaCl background (− 1.3 V), so this wave was due to the decomposition of the background. The 1st cathodic wave corresponded to the reduction of Zn^{2+}.

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Fig. 1 CV of graphite electrode ($0.35\ \mathrm{cm}^2$) in urea-NaCl-$ZnCl_2$ ($0.18\ \mathrm{mol \cdot L^{-1}}$) at 125 ℃, $0.050\ \mathrm{V \cdot s^{-1}}$

The anodic peak was due to anodic solution of zinc. If sweep backed at the potential slightly negative to − 1.06 V, a narrow anodic stripping peak appeared and the slope of the line crossed the zero current axis was very high. These results indicate that electrodeposition of metal was reversible[4].

Fig. 2(a) is the voltammogram of Zn^{2+} reduced on Ti electrode in urea-NaCl-$ZnCl_2$ melt at different potential sweep rates. The peak potential of the cathodic wave did not change with the sweep rate. The relation of the peak current and the square root of the sweep rate was linear (Fig. 2(b)).

For the reversible charge transfer with insoluble electrode product, the peak current equation is as follows[5]:

$$I_p = 0.611(nF)^{3/2}(Dv/RT)^{1/2}AC \qquad (1)$$

From the slope of the line in Fig. 2(b) and equation (1), the diffusion coefficient of Zn^{2+} in urea-NaCl-$ZnCl_2$ at 125 ℃ was calculated as $1.31 \times 10^{-6}\ \mathrm{cm^2 \cdot s^{-1}}$.

3.1.2 Current-time curve at potential step

The current-time curves of graphite electrode in urea-NaCl-$ZnCl_2$ melt at different potential steps are shown in Fig. 3(a). The $I \sim t$ curves at the potential of − 1.05 V and − 1.10 V overlapped together. The plot of $I \sim t^{-1/2}$ was a linear line (Fig. 3(b)) which accords with the cottrell equation[6]:

$$I = nF(D/\pi t)^{1/2}AC \qquad (2)$$

This result indicates that electroreduction of Zn^{2+} was controlled by diffusion. From the equation (2) and the slope of the line in Fig. 3(b), diffusion coefficient of Zn^{2+} in the melt was calculated as $1.01 \times 10^{-6}\ \mathrm{cm^2 \cdot s^{-1}}$ (125 ℃) which approximated to the value of D calculated from the linear sweep potential voltammogram.

3.2 *Electroreduction of* Ni^{2+}

3.2.1 Voltammogram

The cyclic voltammogram of graphite electrode in urea-NaCl-$NiCl_2$ melt at 125 ℃ is shown

Fig. 2 Voltammogram of Ti electrode ($0.90\ \mathrm{cm}^2$) in urea-NaCl-$ZnCl_2$ ($0.18\ \mathrm{mol \cdot L^{-1}}$) at 125 ℃ (a) and plot of $I_p \sim v^{1/2}$ (b)

1 — $v = 0.02$ V/s; 2 — $v = 0.05$ V/s; 3 — $v = 0.10$ V/s; 4 — $v = 0.20$ V/s

Fig. 3 **$I \sim t$ curves of graphite electrode (0.40 cm^2) in urea-NaCl-$ZnCl_2$ (0.18 mol·L^{-1}) at 125 ℃ (a) and plot of $I \sim t^{-1/2}$ (b)**

1 — E = 0.95 V; 2 — E = 1.05 V; 3 — E = 1.0 V

Fig. 4 **CV of graphite electrode in urea-NaCl-$NiCl_2$(0.12 mol·L^{-1}) at 125 ℃ (a), voltammogram of Cu electrode (0.47 cm^2) (b) and plot of $I_p \sim v^{1/2}$ (c)**

Table 1 **The αn_a and α of Ni^{2+} + 2e= Ni**

v/V · s^{-1}	$\vert E_p - E_{p/2}\vert$ / V	αn_a	α
0.020	0.065	0.98	0.49
0.050	0.069	0.92	0.46
0.100	0.070	0.91	0.47
0.200	0.070	0.91	0.47
	average:	0.93	0.47

in Fig. 4(a). The cathodic wave started at − 0.6 V and the anodic wave started at − 0.2 V when the potential sweep back. Fig. 4(b) is the voltammogram of Ni^{2+} reduced on Cu electrode in urea-NaCl-$NiCl_2$ melt at different sweep rates. The peak potential changed with the sweep rate. Electrolysing with Cu electrode in this melt at about − 0.8 V, a lustrous grey metal layer covered the Cu electrode which indicated that nickel was deposited. Hence, the reduction of Ni^{2+} to nickel was irreversible in one step.

For the irreversible charge transfer, the peak potential and the half peak potential has the following relation[6]:

$$|E_p - E_{p/2}| = 1.857RT/\alpha n_a F \qquad (3)$$

From the data of $|E_p - E_{p/2}|$ in Fig. 4(b) and the equation (3), the average αn_a was calculated as 0.93 and the α was determined as 0.47.

The relation of peak current and potential sweep rate is[6]

$$I_p = 0.4958nF(\alpha n_a FDv/RT)^{1/2}AC \quad (4)$$

According to equation (4) and the slope of the line in the Fig. 4(c), the diffusion coefficient of Ni^{2+} in the melt was calculated as 1.87×10^{-6} cm^2·s^{-1}(125 ℃).

3.2.2 Current-time curve at potential step

Fig. 5(a) is the current-time curves of graphite electrode in urea - NaCl - $NiCl_2$ at 125 ℃. After charging the double layer at first, the currents did not decrease monotonously, but increased gradually. This is the character of nucleation and growth. Later, the currents decreased because of the diffusion of the Ni^{2+} ions.

The relation of I and $t^{1/2}$ was linear(Fig. 5(b)), which agreed with[7]

$$I = nF\pi(2DC)^{3/2}M^{1/2}\rho^{-1/2}Nt^{1/2} \qquad (5)$$

where N is initial crystal nuclear number; M is molecular weight; ρ is deposit density.

Fig. 5 $I \sim t$ curves of graphite electrode in urea-NaCl-$NiCl_2$ (0. 12 mol·L^{-1}) at 125 ℃ (a), and plot of $I \sim t^{1/2}$ (b)

Fig. 6 CV of graphite electrode (0. 49 cm^2) in urea-NaCl-$CuCl_2$ (0. 19 mol·L^{-1}) at 125 ℃ (a), and $I_p \sim v^{1/2}$ of 1st cathodic peak (b)

1 — v = 0. 02 V/s; 2 — v = 0. 05 V/s; 3 — v = 0. 10 V/s; 4 — v = 0. 20 v/s

Therefore, the formation of crystal nucleus proceeded instantaneously. The positive delayed loop (i. e. the reduction current at cathodic sweep is smaller than that at sweep back) appeared on the cyclic voltammogram (Fig. 4(a)), which showed the crystal polarization existed. This phenomenon agreed with the $I \sim t$ curve.

3. 3 *Electroreduction of* Cu^{2+}

Fig. 6 (a) is the cyclic voltammogram of graphite electrode in urea -NaCl-$CuCl_2$ at 125 ℃. Two cathodic waves started at + 0. 35 V and − 0. 55 V respectively and two peak currents were almost equal. These results indicate the electroreduction of Cu^{2+} is two steps with the same charge transfer number, i. e. $Cu^{2+} + e = Cu^{+}$, $Cu^{+} + e = Cu$.

Two anodic peaks in the Fig. 6(a) corresponded to the opposite processes of the two cathodic steps. The peak potentials of the two cathodic peaks did not change with the sweep rates and the $I_p \sim v^{1/2}$ was linear (Fig. 6(b)). Hence,

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Table 2 shows the effect of the amount of the reducing agent on the rate of TiO_2 reduction. The results indicated that the rate of TiO_2 reduction increased with increasing amount of reducing agent. According to Eqn. (2), $C(Si)$ is the factor that influenced the rate of TiO_2 reduction.

5 CONCLUSIONS

(1) The decrease of the rate of silicothermic reduction of TiO_2 in TiO_2 containing slag melt takes place throughout the reduction process. It is no use prolonging the reduction time since very little TiO_2 will be reduced after 60 min.

(2) For an initial TiO_2 content of 23.5 percent, the rate of silicothermic reduction of TiO_2 in TiO_2 containing slag increases with increasing reduction temperature.

(3) An increase in the TiO_2 content in TiO_2 containing slag generally causes an increase in the rate of reduction of TiO_2.

(4) The amount of reducing agent is a factor that accelerates the rate of silicothermic reduction of TiO_2 in TiO_2 containing slag melt.

(5) The kinetic parameters of the silicothermic reduction of TiO_2 in TiO_2 containing slag melt are given by $C(TiO_2) = C(TiO_2)_0 e^{-k't}$, where $C(TiO_2)_0 = 23.5\%$, $k' = 0.025$.

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electroreduction of Cu^{2+} to Cu is reversible with two steps.

For the reversible charge transfer with soluble product, the relation of peak current and sweep rate is as follows[6(d)]:

$$I_p = 0.4463(nF)^{3/2}(Dv/RT)^{1/2}AC \quad (6)$$

From the slope of line in Fig. 6(b) and the equation (6), the D of Cu^{2+} was calculated as $1.27 \times 10^{-6}\ cm^2 \cdot s^{-1}$ (125 ℃).

4 CONCLUSIONS

(1) The electroreduction of Zn^{2+}, Ni^{2+} and Cu^{2+} has different kinetic characters. The charge transfer of Zn^{2+} is reversible in one step. The charge transfer of Ni^{2+} is irreversible in one step. The charge transfer of Cu^{2+} is reversible with two steps.

(2) The diffusion coefficients of Zn^{2+}, Ni^{2+} and Cu^{2+} in urea-metal chlorides melt were determined. The order of magnitude of D is $10^{-6}\ cm^2 \cdot s^{-1}$ (125 ℃).

(3) The transfer coefficient α of electrode reaction: $Ni^{2+} + 2e = Ni$ was determined as 0.47.

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