

Anodic reaction kinetics of electrowinning zinc in system of Zn(II)-NH₃-NH₄Cl-H₂O^①

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Abstract: The anodic reaction kinetics of zinc electrowinning was investigated on the titanium base RuO₂ anode in the system of Zn(II)-NH₃-NH₄Cl-H₂O. The effects of stirring speed, ammonium chloride concentration and temperature on anodic reaction rate were studied through the curve measurement of potentiostatic polarization. The results reveal that the electrochemically controlled anodic reaction obeys Tafel equation and the anodic reaction order for ammonium chloride is 1.056, with the apparent activation energy of 40.17 kJ/mol. The general equation of anodic reaction kinetics was obtained.

Key words: zinc electrowinning; anodic reaction; kinetics; Ti/RuO₂ anode

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1 INTRODUCTION

In the present world, eighty percent of zinc output is extracted by hydrometallurgical method, in which zinc is electrowinned in the system of ZnSO₄-H₂SO₄-H₂O with high power consumption of about 3 100 kW·h per tone zinc. In zinc electrowinning process, alloys^[1-3], such as Pb-1% Ag alloy or Pb based multi-component alloy, were used as anode. These anodes bring forth some disadvantages, such as lead polluting zinc, higher over-potential and restricted chloride concentration. EZINEX process^[4-6] utilizes the high concentrated ammonium chloride solution to leach electric arc furnace (EAF) flue dust of steel mill, and zinc with 99.0% - 99.5% purity is electrowinned from cemented solution using titanium cathode and graphite anode. However, the electrode distance becomes increasingly wider and the anodic mud has to be cleaned up regularly for the graphite anode has lower conductivity and scraps off easily. RuO₂ coated titanium anode, which has advantages of good electrocatalysis to chloride, low over-potential^[7,8], easily improving current density and decreasing oxygen evolution^[9], has been used to sodium chloride electrolysis in chloride-alkali industry.

The thermodynamics^[10], optimum electrowinning conditions and anodic mechanism^[11] in the Zn(II)-NH₃-NH₄Cl-H₂O system were previously studied. On the basis of these studies, the renovated process was successfully used to treat zinc calcine and zinc oxide flue dusts of lead smelting, and to produce

zinc with high purity^[12,13]. Compared with the traditional hydrometallurgical method, this process possesses shorter flow sheet, lower power consumption and higher product quality. Lessoned from the successful experiences of chloride-alkali industry, the titanium base RuO₂ plank was used as anode for zinc electrolysis in the system of Zn(II)-NH₃-NH₄Cl-H₂O. In this article, the anodic reaction kinetics of zinc electrowinning in the system of Zn(II)-NH₃-NH₄Cl-H₂O was studied.

2 EXPERIMENTAL

2.1 Equipment and reagents

The titanium base RuO₂ anode was afforded by Northwest Institute for Nonferrous Metal Research, which, determined by electron energy spectrum analyzing, was composed of titanium 65.70%, ruthenium 31.81% and iron 2.49%. The test equipment of model 273, programmed with electrochemical software of power CV, 270, M352, etc, was produced by EG&G Princeton Applied Research Corporation. The electrochemical measurement was performed in a three electrodes cell of 400mL with a saturated calomel reference electrode and high purity zinc cathode, and the anode and cathode areas are all 1 cm².

The chemicals, ZnO, NaOH, NH₄Cl, NaCl, NH₄NO₃ and concentrated ammonia solution, are all analytic reagents. The simulated electrolyte of 5 L was prepared by adding 125 g ZnO to 300 mL concentrated ammonia solution and about 3.5 L distilled

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water to form the solution, which contains 19.75 g/L zinc and 4.93 mol/L chloride.

2.2 Experimental methods

2.2.1 Experiments of determining ion participated in anodic reactions

Several solutions were prepared as the following procedures respectively. Firstly, 0.5 L Zn(II)-NH₃-NH₄Cl solution was prepared by mixing ZnO 12.5 g, NH₄Cl 134 g and 35 mL of concentrated ammonia water, whose pH value was 9.21 determined by the Delta 320 pH meter (Mettler-Toledo Instruments (Shanghai) Ltd). Secondly, 0.5 L sodium chloride solution was prepared by solving NaCl 146.3 g, and the pH value was adjusted to 9.22 by adding sodium hydroxide solution. Thirdly, 0.5 L Zn(II)-NH₃-NH₄NO₃ solution was prepared by mixing ZnO 12.5 g, NH₄NO₃ 200 g, and concentrated ammonia solution 35 mL, and the pH value was adapted to 9.22 by adding nitric acid. To measure the steady-state polarization, the scanning potential was ranged from 0.7 V to 1.5 V (vs SCE), the scanning rate was 2 mV/s and temperature was maintained at 25 °C.

2.2.2 Experiments of determining control step

The stirring rate of 0, 100, 200, 300 r/min was serviced respectively by model JBV-II stirrer. When the steady-state polarization was measured, the scanning potential was ranged from 0.7 V to 1.5 V (vs SCE) and temperature was maintained at 25 °C.

2.2.3 Experiments of determining effects of NH₄Cl concentration on reaction rate

The ammonium chloride solution of 0.4 L with concentration of 2, 3, 4 and 5 mol/L was tested. When the steady-state polarization was measured, the scanning potential was ranged from 0.9 V to 1.8 V (vs SCE) and temperature was maintained at 25 °C.

2.2.4 Experiments of determining effects of temperature on anodic reaction rate

When the steady-state polarization was measured, the scanning potential was ranged from 0.7 V to 1.35 V (vs SCE) and temperature was controlled at 11, 21, 34 and 44 °C respectively.

3 RESULTS AND DISCUSSION

3.1 Determination of ions participated in anodic reactions

Varying the ion species participated in anodic reactions, the current density—potential curves were plotted in Fig. 1.

In Fig. 1, curve 1 was measured when only chloride ion existed. The current density represents the anodic reaction rate. Anodic reaction is performed as

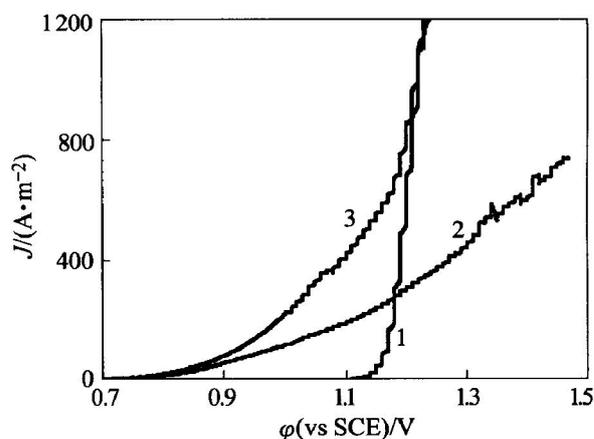


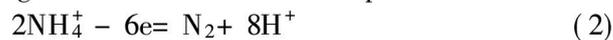
Fig. 1 Current density—potential curve of different ions
1—NaCl; 2—NH₃-NH₄NO₃; 3—NH₃-NH₄Cl

reaction(1) for the overpotential of oxygen evolution is much higher than that of chloride evolution on the Ti/RuO₂ anodic surface^[9].



Curve 1 shows that the anodic reaction hardly takes place when potential is lower than 1.10 V (vs SCE), and the current density increases sharply when potential is higher than 1.15 V (vs SCE). So, we can conclude that a large amount of chloride ions participate in the anodic reaction when the potential is higher than 1.15 V (vs SCE), which is just at the point of chloride evolution potential.

Curve 2 was measured when ammonia, ammonium ion and nitrate ion co-existed. The nitrate ion can not participate in anodic reaction for it can not be oxidized, and no oxygen evolution can take place for the anodic reaction of curve 1 can not take place as the potential is lower than 1.15 V (vs SCE). So, the following anodic reactions are most possible.

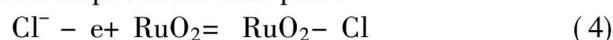


or



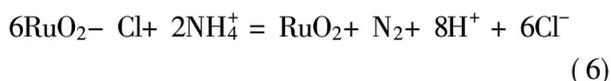
Curve 2 shows that the NH₃ or NH₄⁺ oxidation begins to take place when the potential is higher than 0.7 V (vs SCE), but the anodic reaction rate increases slowly with the anodic potential increasing.

Curve 3 was measured in Zn(II)-NH₃-NH₄Cl-H₂O system. At a certain potential lower than 1.15 V (vs SCE), the anodic reaction rate of curve 3 is much larger than the total rate of curve 1 and curve 2. The nitrogen evolution on the anode was proved in Refs. [11, 14] in the Me(II)-NH₃-NH₄Cl-H₂O system. So, we can presume that among the ammonia, ammonium ion and chloride ion, the following anodic reaction steps should take place.





or



With good catalytic activity, the newly produced chloride can increase the nitrogen evolution of the ammonia and ammonium oxidation, so that the anodic reaction rate increases radically.

3.2 Control step of anodic reaction

The steady-state polarization curves at different stirring speeds are drawn in Fig. 2.

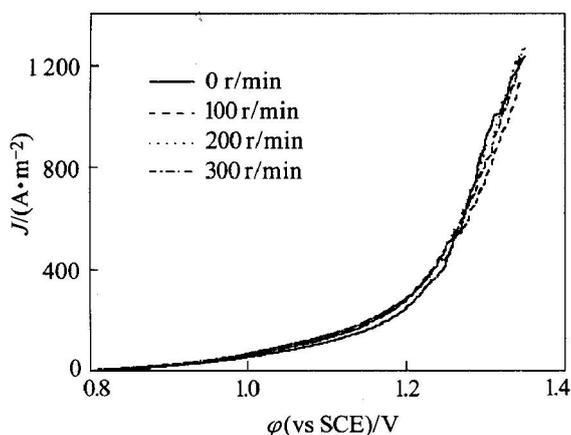


Fig. 2 Steady-state polarization curves at different stirring speeds

Fig. 2 shows that the anodic reaction rate hardly has any change with the stirring speed increasing, so we can conclude that the diffusion speed of the ions participating in anodic reaction doesn't affect the reaction rate, and the anodic reaction is controlled by electrochemical reaction. The curves were dealt with Tafel equation and the results are shown in Fig. 3.

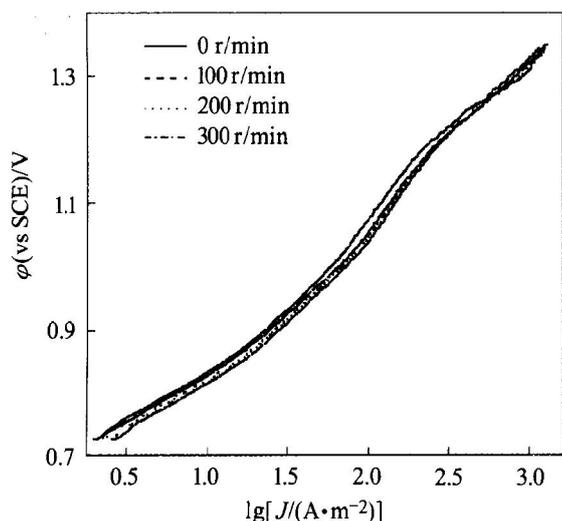


Fig. 3 Tafel curves at different stirring speeds

In the range from 0.7 to 1.3 V (vs SCE), we can consider that the anodic reaction is electrochemically controlled. The linear regression of data under condition of no stirring can be expressed as

$$\varphi_{\text{measured}} = 0.6095 + 0.2366 \lg J \quad (7)$$

Since

$$\varphi_{\text{TD}} = \varphi_{\text{ClO}^-/\text{Cl}^-}^{\ominus} + \frac{nF}{2.303RT} \lg \frac{[\text{ClO}^-]}{[\text{Cl}^-]} + \frac{nF}{2.303RT} \lg [\text{H}^+] \quad (8)$$

where φ_{TD} represents the theoretical decomposition potential. When pH value is 9.22, $\varphi_{\text{TD}} = 1.1695$ V.

At 25 °C the standard electrode potential of saturated calomel electrode (i. e. $\varphi_{\text{SCE}}^{\ominus}$) is 0.2514 V.

$$\eta = \varphi_{\text{measured}} + \varphi_{\text{SCE}}^{\ominus} - \varphi_{\text{TD}} \quad (9)$$

Substitute Eqn. (7), the values of $\varphi_{\text{SCE}}^{\ominus}$ and φ_{TD} into Eqn. (9), the Tafel equation was obtained as:

$$\eta = -0.8114 + 0.2366 \lg J \quad (10)$$

Since $\lg J_0 = -a/b = 0.8114/0.2366 = 3.4294$, the exchange current density (i. e. J_0) is determined as 2687.9 A/m².

3.3 Effects of NH₄Cl concentration on anodic reaction rate

The steady-state polarization curves are shown in Fig. 4, where the concentration of ammonium chloride is 2, 3, 4 and 5 mol/L respectively.

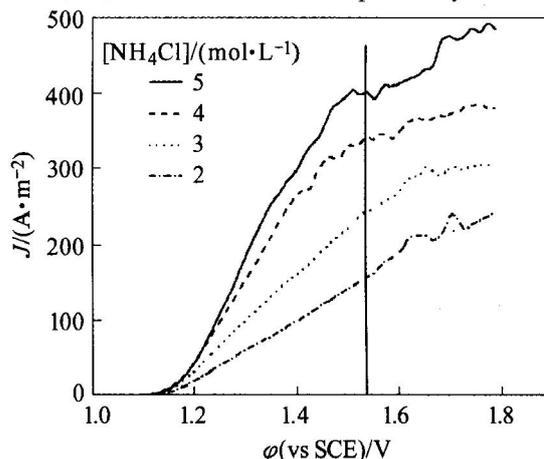


Fig. 4 Steady-state polarization curves at different NH₄Cl concentrations

In Fig. 4, the anodic reaction rate increases with the increasing of ammonium chloride concentration. The relationship between the current density and ammonium chloride concentration can be expressed as following equation when the other conditions remain unchanged^[15].

$$J = k[\text{NH}_4\text{Cl}]^m$$

so

$$\lg J = \lg k + m \lg [\text{NH}_4\text{Cl}]$$

The relationship between $\lg J$ and $\lg [\text{NH}_4\text{Cl}]$

was plotted in Fig. 5.

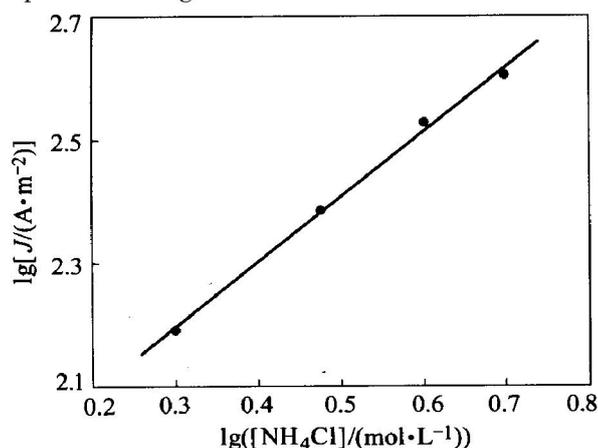


Fig. 5 Order for NH_4Cl anodic reaction

The linear formula is expressed as:

$$\lg J = 1.878 + 1.056 \lg([\text{NH}_4\text{Cl}]) \quad (11)$$

The slope of the line is 1.056, so the order for NH_4Cl anodic reaction is 1.056.

3.4 Effects of temperature on anodic reaction rate

The steady-state polarization curves are shown in Fig. 6, in which the temperature is fixed at 11, 21, 34, 44 °C respectively.

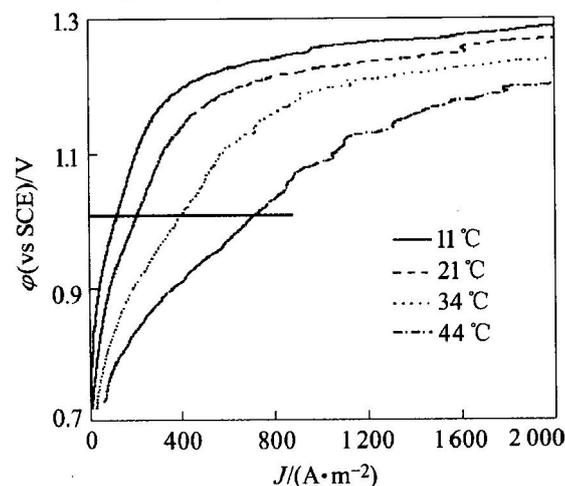


Fig. 6 Steady-state polarization curves at different temperature

According to Ref. [15], the relationship among current density, temperature and apparent activation energy is described as the following equation at an arbitrary fixed potential:

$$\lg J = B - \frac{E}{2.303RT} \quad (12)$$

In practical electrowinning process, temperature is about 37 °C and current density is 400 A/m^2 . So, the potential at the temperature 34 °C and current density 400 A/m^2 is used as the standard value. We can choose the current density at different temperature when the potential is fixed at 1.01 V (vs SCE). The relationship of $\lg J$ and $10^3/T$ is plotted in Fig.

7.

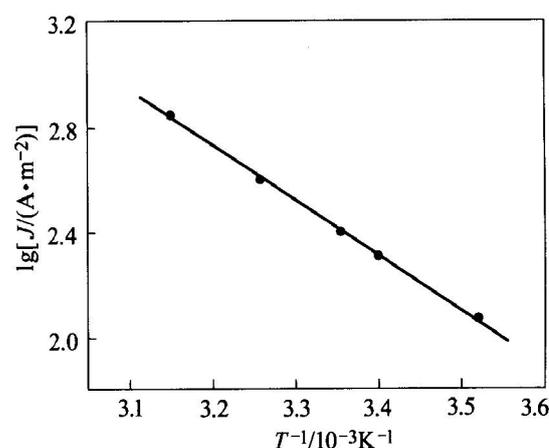


Fig. 7 Relationship of $\lg J$ and T^{-1}

The linear equation of $\lg J$ and T^{-1} was expressed as

$$\lg J = 9.446 - 2.098 \times 10^3 / T \quad (13)$$

From the Eqns. (12) and (13), we can deduce the following equation:

$$2.098 \times 10^3 / T = \frac{E}{2.303RT}$$

so $E = 40.171$ kJ/mol and the apparent activation energy is 40.17 kJ/mol.

4 EQUATION OF ANODIC REACTION KINETICS

On the basis of the effects of parameters on anodic reaction, the anodic reaction rate can be expressed as

$$J = nFk_0[\text{NH}_4\text{Cl}]^m \exp\left(-\frac{E}{RT}\right) \quad (14)$$

where n represents the attained or lost electrons; F is Faraday constant; E is apparent activation energy; m is the reaction orders of ammonium chloride; k_0 is apparent reaction rate constant.

When the ammonium chloride concentration is 1 mol/L, the apparent activation energy is 40.171 kJ/mol, reaction orders is 1.056 and exchange current density is 2687.9 A/m^2 , the apparent reaction rate constant can be figured out to be

$$k_0 = 3.066 \times 10^5$$

So, the general equation of anodic reaction kinetics in the $\text{Zn}(\text{II})-\text{NH}_3-\text{NH}_4\text{Cl}-\text{H}_2\text{O}$ system can be expressed as

$$J_a = 3.066 \times 10^5 \times F[\text{NH}_4\text{Cl}]^{1.056} \times \exp\left(-\frac{40171}{RT}\right) \quad (15)$$

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