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Kinetics of electrochemical process of galena electrode in diethyldithiocarbamate solution①

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[Abstract] The electrode process of galena in diethyldithiocarbamate (DDTC) solution at pH 11.4 has been investigated using cyclic voltammetry, potentiostatic and chronopotentiometry. Electrodeposit of PbD_2 on galena electrode surface can occur while the electrode potential is higher than - 0.05 V. The relationship between the current density caused by diffusion and reaction time has been ascertained, and the diffusion coefficient of DDTC on galena surface in DDTC solution is about 1.12×10^{-6} cm^2/s. A passive PbD_2 film covers the surface of galena electrode.

[Key words] electrode process; galena; electrochemistry of flotation
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1 INTRODUCTION

Diethyldithiocarbamate (DDTC) is one of the most frequently used collectors for flotation of heavy-metal sulfide minerals, such as galena, chalcopyrite and jamesonite, and it shows strong selectivity[1]. When DDTC was used in highly alkaline (pH> 11.4) for separating galena from sphalerite and pyrite[2], it was a powerful collector for galena, but a weak collector for pyrite and sphalerite.

The oxidation and decomposition mechanism of xanthate or diethyldithiocarbamate (DDTC) on different sulfide minerals in the presence of oxidants such as oxygen, chlorite, hypo-chlorite, bromine and iodine at different pH levels have been reported[3]. But very few references were available on xanthate or diethyldithiocarbamate decomposition in highly alkaline (pH> 11.4) solution[4].

Knowledge of reactions that occur on mineral surface in aqueous diethyldithiocarbamate solution is very important, because there exist many convincing evidences with regard to the significance of pulp potential to the flotation of sulfide minerals and precious metals[5, 6]. It is well established that the development of hydrophobicity on sulfide minerals arises from an anodic process of collector, which is coupled with a catholic process such as reduction of oxygen[7, 8]. Since the anodic reaction gives rise to the hydrophobic character of the mineral surface, a clear relationship between the potential and flotation recovery exists in various flotation systems[9, 10]. It is important and essential to determine the kinetics parameters of electrode process of DDTC on sulfide mineral surface from both scientific and practical points of view. No systematic study of electrode process with DDTC on galena surface has been reported, although the reagent was widely used in flotation for sulfide minerals. To improve the efficiency of DDTC used in flotation, it is essential to understand the mechanism involved in the decomposition of DDTC on galena surface, more specifically, to establish the kinetics equilibrium and transfer coefficient of DDTC ion on galena surface.

This investigation was undertaken to study a galena-DDTC system to get better insight into the mechanism of electrodeposition of DDTC ion on mineral surface.

2 EXPERIMENTAL

The galena sample used in this study was supplied by Fankou Mine of Guangdong Province. The purity of the galena is 96.1%. Section cut out from the highly mineralized mineral was fashioned into the form of electrode for electrochemical measurement. The cut section of sulfide mineral was mounted on the tip of a perspex tubule of d7 mm sealed by epoxy resin and the exposed outer surface was well polished. Electrical connection was achieved through a copper wire soldered onto the surface of sulfide mineral. The exposed surface area of the electrode was about 1 cm^2. Potentiostat Model 273A was used in all electrochemical measurements. The EG&G electrochemical analysis system (Princeton Applied Research Model 270) was used for the analysis of electrochemical experiment results. The electrochemical experiments were carried out in a three-compartment cell, including a graphite counter electrode, galena electrode and saturated calomel reference electrode (SCE). During the

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experiments, an oxygen-free nitrogen atmosphere was maintained over the electrolyte to prevent oxygen ingress.

3 RESULTS AND DISCUSSION

In DDTC solution, the anodic reactions on galena surface may take place as follows:

$$PbS \longrightarrow Pb^{2+} + S^0 + 2e \quad (1)$$

$$PbS + 2D^- \longrightarrow PbD_2 + S^0 + 2e \quad (2)$$

$$2PbS + 4D^- + 2H_2O \longrightarrow 2PbD^2 + S_2O_3^{2-} + 6H^+ + 8e \quad (3)$$

In alkaline solution, the concurrent cathodic reduction of oxygen would occur on galena surface:

$$(1/2)O_2 + H_2O + 2e \longrightarrow 2OH^- \quad (4)$$

3.1 Cyclic voltammetry

Fig. 1 shows the voltammograms in pH 11.4 buffer for a freshly ground, stationary galena electrode in the presence of DDTC starting from − 0.75 V(SHE) in the positive direction. The programmed scan is cycled for three times. The current density increases abruptly when the potential is higher than − 0.05 V, which is assigned to the oxidation of DDTC on galena surface as reaction (2). With the increase of cycle number, the anode current decreases, which shows that PbD_2 resides on galena surface, and little can be reduced at negative potential.

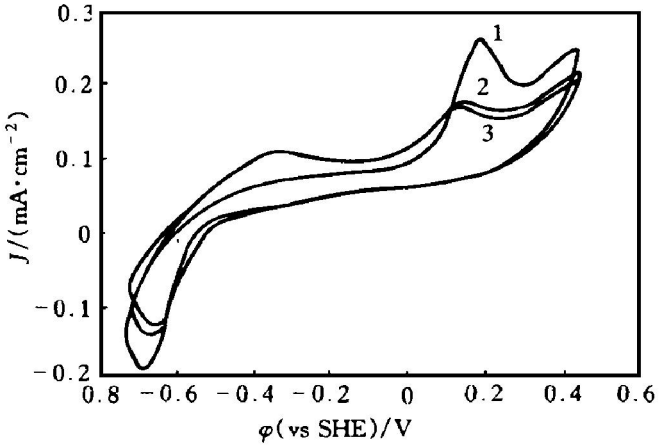

Fig. 1 Voltammetry curves of a galena electrode in presence of DDTC ([DDTC⁻] = 10^{-4} mol/L, pH= 11.4, 25 ℃, scan rate 20 mV/s)

The second anode shoulder of all cycles is close to 0.3 V, which is assigned to the electrodeposition of DDTC on galena surface as reaction (3). The anodic process of galena electrode is inhibited by the residuary PbD_2 adsorbed on its surface. It is demonstrated that the electrodeposit of PbD_2 on galena surface occurs when the electrode potential is higher than − 0.05 V. From Fig. 1, the cathodic current increases abruptly while the electrode potential is lower than − 0.45 V, and it is shown that the PbD_2 is stable on the electrode surface.

3.2 Determination of diffusion coefficient of DDTC on galena surface

In potentiostatic experiment, the potentiostat applies a constant potential for a special duration and monitors the resulting current density, which can be used to investigate electrode process and to determine the diffusion coefficient of DDTC. From Fig. 1, there is a space of 0.8 V between the anodic shoulder and cathodic shoulder, and it is determined that the production of PbD_2 on galena surface is an irreversible reaction. Fig. 2 shows the plot of current density versus time for galena electrode in DDTC solution in response to potentiostatic step 0.10 V. The relationship between current density and time can be ascertained by the following equation:

$$J^{-1} = -4.16 \times 10^{-3} + 1.61 \times 10^{-2} t^{0.5} \quad (5)$$

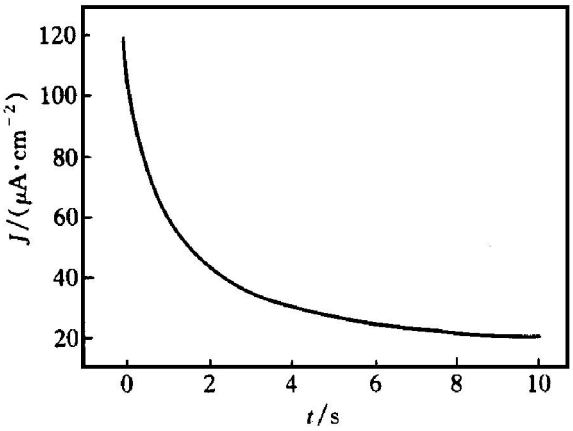

Fig. 2 Current and time change in response to potentiostatic step for galena electrode ([DDTC⁻] = 10^{-4} mol/L, pH= 11.4, 25 ℃)

From an electrochemical reaction in the electrolyte solution, the suppositions are given as follows:

1) Diffusion of reactant obeys the second Fick law, the current caused by diffusion of reactant is directly proportional to the superficial area of electrode surface;

2) The electrode process is controlled by diffusion of reactant;

3) The electromigration and convection are neglected.

The boundary conditions are determined as follows.

1) The concentration of DDTC in the system is equal to the initial concentration, i.e. $c_D(x, 0) = c_D^0$.

2) The concentration of DDTC at indefinite position away from the electrode is equal to the initial concentration, which is described by $c_D(\infty, t) = c_D^0$.

3) The concentration of DDTC on the surface of electrode is equal to 0, expressed by $c_D(0, t) = 0$.

The current density caused by diffusion can be given by the following equation,

$$J = nFD\left[\frac{\mathrm{d}c_D(x,t)}{\mathrm{d}x}\right]_x = 0 \quad (6)$$

According to the second Fick law, the following equation can be obtained:

$$c_D(x,t) = c_D^0 \mathrm{erf}\left[\left[\frac{x}{2(Dt)^{0.5}}\right]\right] \quad (7)$$

$$J = nFc_D^0\left[\frac{D}{\pi t}\right]^{0.5} \quad (8)$$

$$J^{-1} = (nFc_D^0)^{-1}\left[\frac{\pi t}{D}\right]^{0.5} \quad (9)$$

where D is the diffusion coefficient of DDTC, c_D^0 the initial concentration of DDTC, t the reaction time, n the numbers of transfer electrons in reaction.

The relationship of current density and time in Eqn. (5) can be simplified as

$$J^{-1} = 1.61 \times 10^{-2} t^{0.5} \quad (10)$$

According to Eqns. (9) and (10), the diffusion coefficient of DDTC on galena electrode surface can be determined, and it is about 1.12×10^{-6} cm^2/s.

3.3 Adsorption of PbD_2 on galena electrode surface

From Fig. 2, we can get the relationship between the current density (J) and the reaction time (t) as Eqn. (5). When the applied potential steps to a potential of 0.1 V for duration, the current in the J-t plot trends towards smooth. We can integrate the current density (J) over the reaction time (t) from 0 to 10 s, and the value of total charge (Q) of reaction is about 1 180.4 μC/cm^2. The lattice parameters of galena is 5.936 Å, and the consumed charge per molecule layer of PbD_2 is about 90.8 μC/cm^2. The roughness of galena electrode is assumed to be 5. So we can determine that the thickness of PbD_2 layer adsorbed on galena electrode is 2.6 molecule layers.

3.4 Stability of PbD_2 in alkaline solution

In chronopotentiometry experiment, the potentiostat applies a constant current for a specified duration and monitors the resulting potential, which can be used for many different types of analyses or to investigate electrode kinetics such as the dynamics of reduction of PbD_2 adsorbed on galena surface in highly alkaline solution, which is important for cleaning flotation of galena.

The reduction of PbD_2 adsorbed on galena surface is shown in reaction (11), and it is an irreversible reaction.

$$PbD_2 + S + 2e \longrightarrow PbS + 2D^- \quad (11)$$

For this reaction, the following suppositions are given:

1) The electromigration and convection are neglected;

2) The variations of DDTC concentration are caused by diffusion of DDTC ion.

The relationship between overpotential of cathodic reduction of PbD_2 and the reaction time can be ascertained by the following equation:

$$\eta_R = \frac{2.303RT}{\alpha nF}\lg\frac{J_k}{J_0} - \frac{2.303RT}{\alpha nF}\lg\left[1 - \left[\frac{t}{\tau}\right]^{0.5}\right] \quad (12)$$

where η_R is the overpotential of reaction (11), T the temperature, J_k the galvanostatic current density, J_0 the exchange current density, τ the transition time, t the time of reduction reaction, and α the transmission coefficient.

Fig. 3 shows the resulting curve of chronopotentiometry for a galena electrode in DDTC solution. It gives the plot of potential vs time in response to -200 μA/cm^2 galvanostatic step for electrode. From Fig. 3, we can get the value of the transition time (τ), which is about 5.9 s. The thermodynamic potential (φ) of reaction (11) can be calculated by Nernst Equation while the concentration of DDTC is 10^{-4} mol/L:

$$\varphi = -0.301 - 0.059\lg[\mathrm{DDTC}^-] = -0.065\ \mathrm{V\ (vs\ SHE)}$$

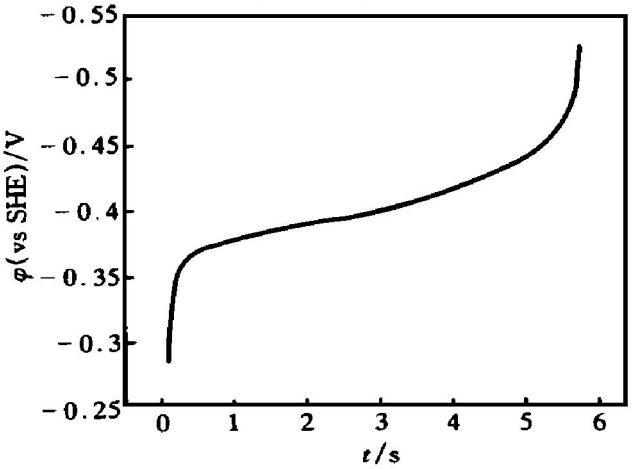

Fig. 3 Potential vs time plot in response to galvanostatic step for galena electrode ([DDTC$^-$] = 10^{-4} mol/L, pH = 11.4, 25 ℃)

From Fig. 3, the electrode potential (φ_h) can be obtained at anytime from 0 to 5.9 s. The overpotential of reaction(11) can be calculated by the following equation: $\eta_R = \varphi_0 - \varphi_h$. Fig. 4 shows the resulting curve of overpotential η_R and the time in response to -200 μA/cm^2 galvanostatic step, and gives the plot of over potential (η_R) vs lg[$1-(t/\tau)^{0.5}$]. The relationship between η_R and lg[$1-(t/\tau)^{0.5}$] can be expressed by

$$\eta = 0.297 - 0.068\lg[1 - (t/\tau)^{0.5}] \quad (13)$$

It is the electrochemical dynamics equation of the reduction of PbD_2 on galena surface. Because the values of R, T, F, J_k and τ are certain, the electrochemical kinetics parameters can be calculated from Eqns. (12) and (13), $J_0 = 8.58 \times 10^{-3}$ μA/cm^2, $n = 2$, $\alpha = 0.435$. From Eqn. (13), when the reaction time is zero, the initial overpotential of reduction of

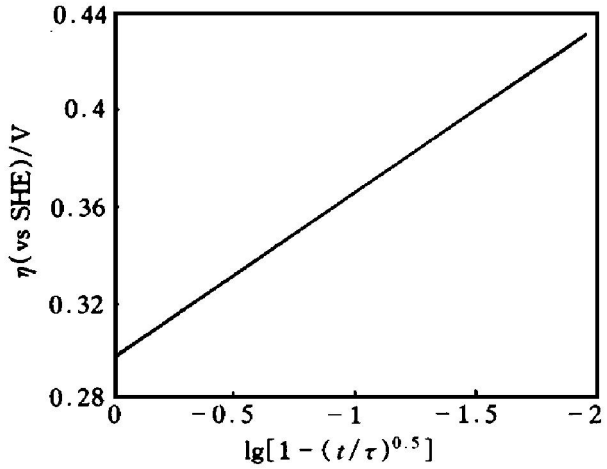

Fig. 4 Relationship between overpotential and $\log[1-(t/\tau)^{0.5}]$ of galena electrode ($[DDTC^-]=10^{-4}$ mol/L, pH= 11.4, 25 ℃)

PbD_2 is 0.297 V. The value of initial overpotential is relatively higher and the value of exchanger current density (J_0) is relatively small enough. The results demonstrate that it is difficult the PbD_2 adsorbed on galena surface to reduce. In other words, the PbD_2 adsorbed on galena surface is stable. So the galena can be floated well in DDTC solution and has a good cleaning floatability. This result of electrochemical experiment agrees with the practice of flotation of galena in DDTC solution.

4 CONCLUSIONS

1) The results of cyclic voltammetry demonstrate the electrodeposit of PbD_2 that occurs on galena surface, and the PbD_2 adsorbed on galena surface can not be reduced in the negative direction.

2) The thickness of PbD_2 adsorbed on galena surface at pH 11.4 is about 2.6 molecule layer.

3) The electrochemical dynamics equation of the reduction of PbD_2 adsorbed on galena surface can be ascertained as

$$\eta = 0.297 - 0.068 \lg[1-(t/\tau)^{0.5}]$$

The electrochemical kinetics parameters can be calculated, the exchange current density $J_0 = 8.58 \times 10^{-3}$ μA/cm^2, and the transmission coefficient $\alpha = 0.435$. It is shown that the PbD_2 can be steadily adsorbed on galena surface.

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