Electrochemical oxidation of pyrrhotute in aqueous solution ①

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Abstract: The anodic surface oxidation of natural pyrrhotite in 0. 3 mol/ L KCl and HCl solution (pH 4. 0) and 0. 1 mol/ L $Na_2B_4O_7$ solution (pH 9. 18) respectively was investigated by using cyclic voltammetry, T afel plot, and chronoamperometry. In 0. 3 mol/ L KCl and HCl solution (pH 4. 0) , at potential less than 0. 5 V(vs SHE) , the production of anodic oxidation on pyrrhotite surface can not maintain a stable phase to form a passive film. In 0. 1 mol/ L $Na_2B_4O_7$ solution (pH 9. 18) , when the electrode potential increases to more than 0. 5 V (vs SHE) , part of S is oxidized to sulfate, making the passive film somewhat porous, but elemental S and metal oxidates Fe(OH) $_3$ still remain on the electrode surface, and the passive film can not be broken down totally. According to PARCalc Tafel analysis, the corresponding corrosion current density (J_0) is 5. 34 μA/ cm^2, which is also the exchange current density of the oxidation reaction on pyrrhotite electrode surface in 0. 1 mol/ L $Na_2B_4O_7$ solution (pH 9. 18) . The electrochemical dynamics equation of the oxidation was determined.

Key words: pyrrhotite; electrochemical oxidation; aqueous solution; electrochemistry

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1 INTRODUCTION

In Guangxi Province of China, complex sulfide ores exist, which is the major source of zinc, lead, antimony and tin. The valuable minerals include marmatite (ZnFeS) , jamesonite and cassiterite (SnO_2) , which are associated with a greater abundance of pyrrhotite[1].

Pyrrhotite ($Fe_{1-x}S$) is a kind of non-stoichiometric sulfur rich compound compared with stoichiometric FeS, whose chemical components are not fixed[2]. The iron atom of in pyrrhotite is imperfect, the structural formula could be illustrated as $Fe_{1-x}S$ ($x = 0－0. 223$) , while x is equal to zero the iron atom is perfect in the crystal, the only example is troilite. The reason for the imperfect crystal of pyrrhotite is commonly considered to be that part of Fe^{2+} is oxidized to form $Fe_{x/3}^{2+}Fe_{(x/3}^{3+}S$. Pyrrhotite forms a defect structure with a deficiency of iron with respect to sulfur, terminating in a monoclinic structure Fe_7S_8. Some iron in pyrrhotite presents as Fe^{3+} that stabilizes the lattice[3]. And it was considered that this stabilization changed with the decrease of rest potential of pyrrhotite as iron content increased, indicating that "iron-rich" pyrrhotite is more reactive than Fe_7S_8. When the iron content increases from 46% to 50%(mole fraction) the measured rest potential of natural and synthetic pyrrhotite at pH 3. 0 decreased from $-0. 1$ to $-0. 6 V(vs SHE)$.

Pyrrhotite oxidation has been extensively studied, and it is generally believed that the oxidation of both the mineral and the collector play important roles in flotation process. Majima and Peters[4] defined that pyrrhotite as the most reactive sulfide for a wide range of minerals in acid solution according to the oxidation rate of pyrrhotite with pressurized O_2. Burkin[5] considered that in alkaline solution the pyrrhotite could be coated with the iron oxide that was pseudomorphic with the original sulfide lattice. The iron oxide formed a coherent layer in which slow, solid-state diffusional processes controled its oxidation process. But very few references were available on the electrochemistry kinetics of oxidation happening on pyrrhotite surface in aqueous solution, and few researches are carried out on how the oxide layer modulates the oxidation kinetics of the pyrrhotite. Buckley and Woods[6] thinks it a solid state diffusinal process in which S^{2-} ion moves through the oxide layer for further oxidation on the external surface. This may be the reason why the surface of pyrrhotite can be rapidly oxidized to form a thin ferric hydroxy-oxide lay which overlays an iron-deficient sulfide lattice.

Therefore the study of reactions occurring on sulfide mineral surface in aqueous solution is important. The effect of pulp potential(φ_p) on the flotation of sulfide minerals and precious metals is commonly considered important[7, 8]. It is well es-

tablished that the development of hydrophobicity or hydrophilicity on sulfide minerals arises from an anodic process which is coupled with a cathodic process such as reduction of oxygen[9, 10]. It is essential to determine the kinetics parameters of electrode process of oxidation of sulfide mineral on the surface, and to deeply understand the mechanism involved in the oxidation on mineral surface, then to establish the kinetics equilibrium of this electrode process and calculate the kinetic parameters[11, 12].

In this paper, the authors aim to study the electrochemical oxidation of pyrrhotite to get better insight into the mechanism of electrode process on pyrrhotite surface.

2   EXPERIMENTAL

Table 1 lists the results of magnetic separation of a pyrrhotite collected from Dachang Mine, Guangxi Province, China. The crystal form of the pyrrhotite is monoclinic. Sections cut out from the highly mineralized pyrrhotite were fashioned into form of electrodes for electrochemical measurements. The tested electrode was mounted on epoxy resin, grounded with SiC paper, then polished with 0. 3 μm and 0. 05 μm alumina. The exposed surface area of the electrode was about 1 cm^2. The mounted electrode was then washed with deoxygenated deionized water to remove the adhering alumina particles.

Table 1   Chemical composition of pyrrhotite after magnetic separation(mass fraction, %)

S	Fe	Si	Zn	Mg	Ca
38. 44	60. 31	0. 75	0. 41	0. 28	0. 51

Two kinds of electrolyte were prepared by using analytical grade KCl and $Na_2B_4O_7$ with deionized water of resistivity larger than $6. 0 \times 10^5 \; \Omega \cdot m$. The electrochemical experiments were carried out in a three-compartment cell, including a graphite counter electrode, pyrite electrode and saturated calomel reference electrode (SCE). All potentials in this study are quoted in volts, with respect to a standard hydrogen electrode (SHE).

An Electronics Potentiostat Model 273A and Model 636 electrode rotator were used in all electrochemical measurements. The EG& G corrosion measurement system (Princeton Applied Research Model 352) and Analysis Software (Model 270) were used for the analysis of electrochemical experimental results.

3   RESULTS AND DISCUSSION

3. 1   Cyclic voltammetry

The cyclic voltammogram curves shown in Fig. 1 is obtained in 0. 3 mol/ L KCl and HCl solution (pH 4. 0) for a freshly grounded surface, stationary pyrrhotite electrode starting from − 0. 20 to 0. 9 V (vs SHE). This indicates that, before the strong oxidation at high electrode potential, there is a pre-wave region (− 0. 20 − 0 V vs SHE), in which the oxidation process occurs at lower rate. There is a weak current density peak at an electrode potential around − 0. 08 V (vs SHE). In this electrode potential region, the primary reactions are as
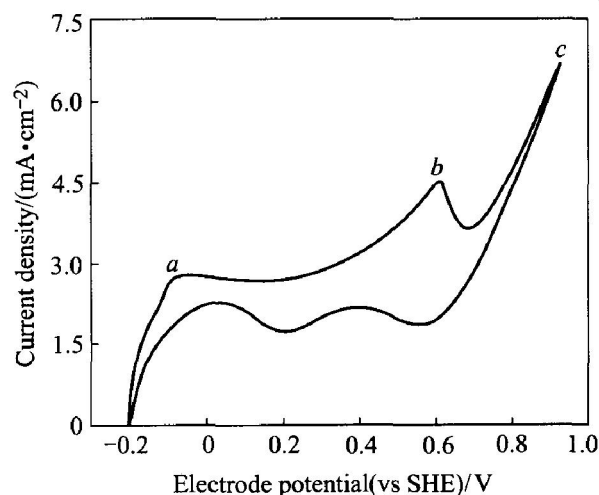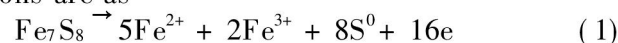
$$Fe_7S_8 \rightarrow 5Fe^{2+} + 2Fe^{3+} + 8S^0 + 16e \qquad (1)$$
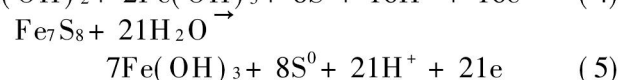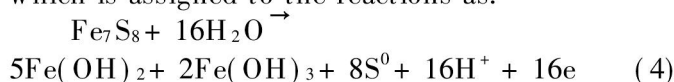$$Fe^{2+} \rightarrow Fe^{3+} + e \qquad (2)$$

Fig. 1   Voltammogram curve of pyrrhotite electrode in 0. 3 mol/ L KCl at 298 K
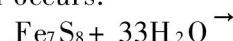(pH= 4. 0, electrode potential sweeping rate: 20 mV/ s)

It shows the production of anodic oxidation can not represent a stable phase at the pyrrhotite surface forming a passive film. When the electrode potential is increased to larger than 0. 5 V (vs SHE), the oxidation current density increases abruptly, indicating that the following reaction can take place:

$$Fe_7S_8 + 12H_2O \rightarrow$$
$$7Fe^{3+} + S_2O_3^{2-} + 24H^+ + 37e \qquad (3)$$
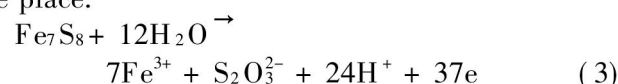
The cyclic voltammogram curves shown in Fig. 2 is obtained in 0. 1 mol/ L $Na_2B_4O_7$ solution (pH 9. 18) in the electrode potential range of − 0. 20 to 0. 9 V (vs SHE). It indicates that, before the main oxidation current density peak, there is a pre-wave region (− 0. 20 − 0. 05 V vs SHE), which is assigned to the reactions as:

$$Fe_7S_8 + 16H_2O \rightarrow$$
$$5Fe(OH)_2 + 2Fe(OH)_3 + 8S^0 + 16H^+ + 16e \qquad (4)$$
$$Fe_7S_8 + 21H_2O \rightarrow$$
$$7Fe(OH)_3 + 8S^0 + 21H^+ + 21e \qquad (5)$$

When the electrode potential is increased to higher than 0. 3 V (vs SHE), the following reaction occurs:
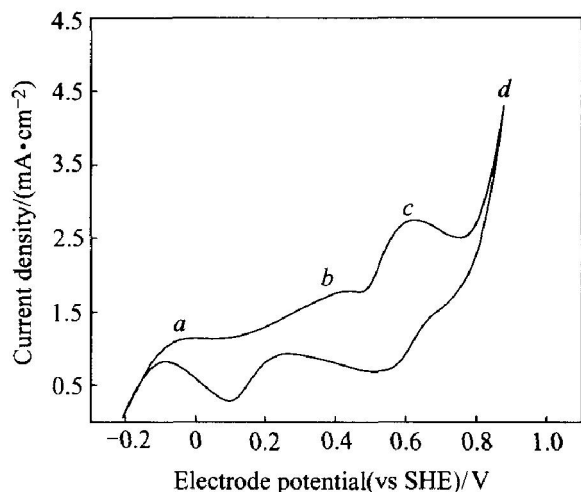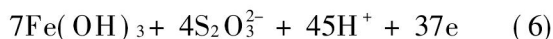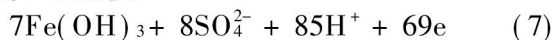
$$Fe_7S_8 + 33H_2O \rightarrow$$

Fig. 2 Voltammogram curve of pyrrhotite
electrode in 0. 1 mol/ L $Na_2B_4O_7$ at 298 K
pH = 9. 18, electrode potential sweeping rate: 20 mV/ s)

$$7Fe(OH)_3 + 4S_2O_3^{2-} + 45H^+ + 37e \qquad (6)$$

When the electrode potential is increased to
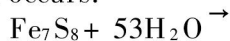higher than 0. 5 V (vs SHE), the following reac-
tion occurs:

$$Fe_7S_8 + 53H_2O \overset{\rightarrow}{}$$

$$7Fe(OH)_3 + 8SO_4^{2-} + 85H^+ + 69e \qquad (7)$$

It is obvious that, in the high electrode poten-
tial region, part of S being oxidized to sulfate can
make the passive film somewhat porous, but the
elemental S and metal oxidates $Fe(OH)_3$ still re-
main on the electrode surface, and the passive film
can not breakdown totally. So the oxidation cur-
rent density of the pyrrhotite in alkaline solution is
smaller than the in acid solution.

3. 2 Tafel plots of pyrrhotite electrode

The Tafel plot of pyrrhotite electrode in 0. 1
mol/ L $Na_2B_4O_7$ solution (pH 9. 18) is shown in
Fig. 3. The entire potential scan is programmed to
start from − 225 mV to 225 mV of rest potential
with a scan rate 0. 2 mV/ s. Using the PARCalc
Tafel analysis, the oxidation rate of pyrrhotite can
be calculated. The corresponding corrosion current
density(J_0) is 5. 34 μA/ cm^2, and it is also the ex-
change current density of the oxidation reaction oc-
curring on pyrrhotite electrode surface.

3. 3 Chronoamperometry

In chronoamperometry, the potentiostat ap-
plies a constant potential for a specified duration
and monitors the resulting current density, which
can be used for many different types of analyses or
to investigate electrode kinetics.

Fig. 4 shows the current density vs time tran-
sients in response to a step in electrode potentials
from rest value to 0. 3, 0. 35, 0. 40, 0. 45 V (vs
SHE), respectively. When the electrode potential
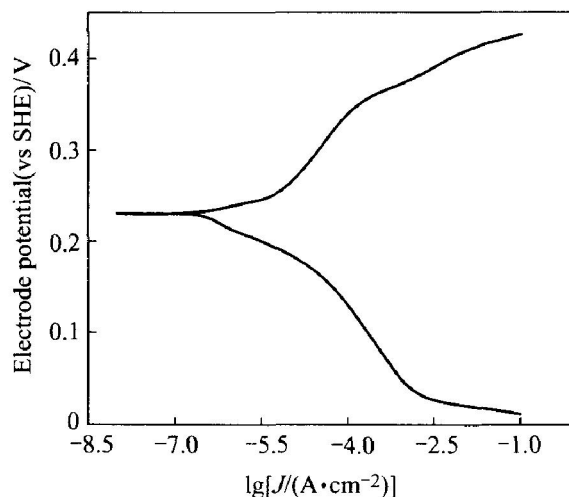increases to higher than 0. 3 V(vs SHE), the half

Fig. 3 Tafel plots of pyrrhotite electrode
in 0. 1 mol/ L $Na_2B_4O_7$ solution (pH 9. 18)

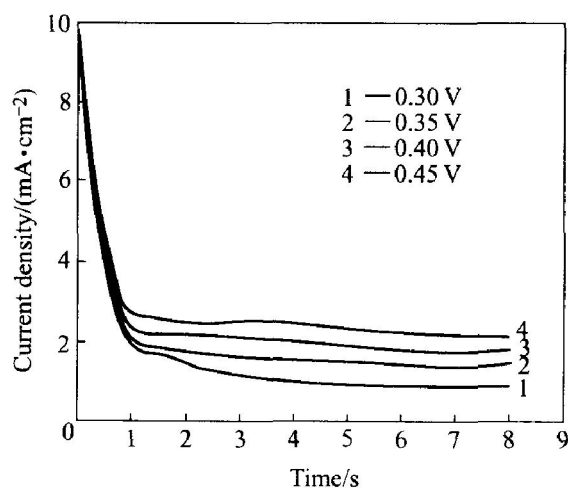**Fig. 4** Curves of current density vs
time stepped from rest potential to
0. 3, 0. 35, 0. 40, 0. 45 V (vs SHE) in
0. 1 mol/ L $Na_2B_4O_7$ at 298K(pH 9. 18)

cell reaction for pyrrhotite in 0. 1 mol/ L $Na_2B_4O_7$
aqueous (pH 9. 18) is assigned to reaction (6).

The relationship between over potential of
reaction (6) and the reaction time can be described
as

$$\eta = [- 2. 303RT/(\beta nF)]\lg J_0 + [2. 303RT/(\beta nF)]\lg J_{t^{\to}0} \qquad (8)$$

where   η is the over potential of oxidation occur-
ring at pyrrhotite electrode surface; T is the tem-
perature(298 K); J_0 is the exchange current densi-
ty; $J_{t^{\to}0}$ is the current density when the concentra-
tion polarization of reaction can not exist; t is the
time of reaction; β is the transmission coefficient;
F is the Farady constant.

The data in Fig. 4 increase approximately line-
arly with the square root of time, as shown in
Fig. 5, from which we can get the value of $J_{t^{\to}0}$, as
about 1. 6, 0. 375, 0. 09, 0. 02 mA/ cm^2, respec-
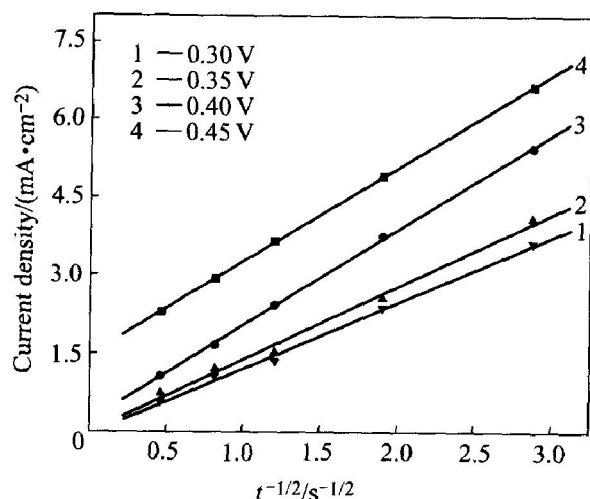tively. Fig. 6 shows the resulting curve of over-

Fig. 5 Relation between current density and square root of time in 0. 1 mol/ L $Na_2B_4O_7$ at 298 K
(Electrode potential is stepped from
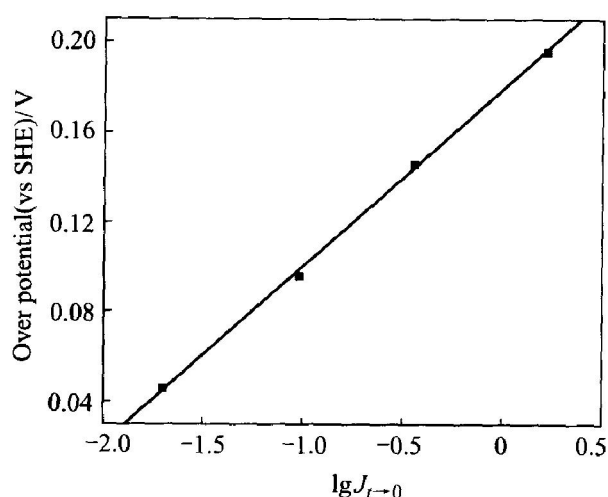rest potential to 0. 3, 0. 35, 0. 40, 0. 45 V(vs SHE))

Fig. 6 Relation between over potential and lg $J_{t \to 0}$

potential η versus $J_{t \to 0}$; it gives the plot of over po-
tential (η) versus lg $J_{t \to 0}$.

So the relationship between η and lg $J_{t \to 0}$ can be expressed by

$$\eta = 0. 18 - 0. 08 \lg J_{t \to 0} \qquad (9)$$

Eqn. (9) is the electrochemical dynamics equa-
tion of reaction(6). Compared with Eqn. (8), the
electrochemical kinetics parameters can be calculat-
ed from Eqn. (9) as $J_0 = 5. 63$ μA/ cm^2, which is
similar to the value got from the Tafel plot.

4 CONCLUSIONS

From the cyclic voltammetry, anodic oxidation
of pyrrhotite in 0. 3 mol/ L KCl and HCl aqueous
(pH 4. 0) and 0. 1 mol/ L $Na_2B_4O_7$ aqueous (pH
9. 18) can not result in passivating a stable film

when the electrode potential is lower than 0. 5 V.
When the electrode potential is increased to more
than 0. 5 V vs SHE, part of the S being oxidized to
sulfate can make the passive film somewhat por-
ous, but the elemental S and metal oxidants still
remain on the electrode surface, and the passive
film can not break down totally. Using the Tafel
plots, the exchange current density of the oxida-
tion reaction occurring on pyrrhotite electrode sur-
face in 0. 1 mol/ L $Na_2B_4O_7$ aqueous (pH 9. 18)
(J_0) was determined as about 5. 34 μA/ cm^2, which
was similar to the value 5. 63 μA/ cm^2 calculated by
chronoamperometry.

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