

Redox Behavior of Chalcopyrite

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Abstract

Electrochemistry of chalcopyrite was investigated using cyclic voltammetry technique at four different pH values. The voltammetry experiments were performed at different anodic switching potentials and scan rates to elucidate the state of reversibility and the kinetics of the electrochemical reactions. The results revealed that oxidation-reduction reactions at chalcopyrite surface were not fully reversible due to irreversible coverage of the surface by iron-hydroxides and/or diffusion of metal ions into solution. The most complicated electrochemical behavior was observed in neutral solution. Most of the elemental sulfur was reduced to H₂S/HS-form at strongly reducing environment. The difference in the kinetics of the anodic and the cathodic reactions was considered as the main reason for this kind of irreversibility. However, the reactions at alkaline pH values were quite clear and have higher degree of reversibility. This was presumably due to stability of the elemental sulfur in the scanning range applied. Most of the elemental sulfur formed during anodic oxidation was involved in reformation of chalcopyrite surface since its reduction potential to HS-form in alkaline solutions is very low and out of the scanning range applied in this study.

Key words: Chalcopyrite, electrochemistry, cyclic voltammetry, pulp potential

INTRODUCTION

Chalcopyrite is the most abundant copper sulfide mineral and is the major commercial source of copper. It has semiconducting property, and reactions occurring on the mineral surface are usually electrochemical in nature in flotation process. Therefore, surface hydrophobicity and flotation performance of chalcopyrite directly depend on pulp potential and redox behavior of chalcopyrite [1-2].

Cyclic voltammetry (CV) is one of the most important electrochemical techniques that has been widely used for the characterization of electrochemically active systems for a long time by electrochemists [3-6]. Cyclic voltammograms are characterized by peak potentials (E_{pc}, E_{pa}) and peak currents (i_{pc}, i_{pa}) of the cathodic and anodic peaks, respectively. For an electrochemically reversible process, the peak separation is given by equation (1). Thus, should be 0.0592/n V for a reversible redox reaction at 25°C with n electrons, or about 60 mV for one electron. Large separation between the oxidation and reduction peaks is indicative of an irreversible process.

$$\Delta E_p = E_{pa} - E_{pc} = \frac{2.303RT}{nF} \quad (1)$$

For a reversible process, peak current increases with an increase in scan rate, but peak potential does not. The increase in the peak current value is a function of the square root of the scan rate according to Randle-Sevcik equation (equation (2)) where i_p is the peak current in amps, A is the electrode area (cm²), D is the diffusion coefficient (cm²/s), c^o is the concentration in mol/

cm³, and v is the scan rate in V/s. Nonlinear increase indicates an irreversible reaction. In addition, larger peak separations at higher scan rates could also be associated with a slow electron transfer and/or changes in the composition of the passive layer [3-5, 7].

$$i_p = 2.69 \times 10^5 n^{3/2} A c^o D^{1/2} v^{1/2} \quad (2)$$

Many research works were conducted on chalcopyrite oxidation by CV. These researches focused mainly on the definition of redox products rather than the kinetics of surface oxidation [1, 8-9]. Iron ions preferentially dissolve as Fe²⁺ in acid solution and form Fe(III) oxide or hydroxide in alkaline conditions at slightly oxidizing potentials. Oxidation of the copper sulfide product also occurs when potential is taken to more positive values. Gardner and Woods [1] obtained redox peaks separated by large potential difference and observed the shift in maximum current density point of anodic peak to lower potentials on chalcopyrite voltammograms at pH 9.2. They explained these findings with the complex nature of chalcopyrite structure, and proposed that the oxidation process was remarkably reversible. However, Chander and Briceno [5] were also obtained such a large difference between redox peaks on pyrite voltammogram at alkaline pH, and related with the irreversibility of redox process. Mishra and Osseo-Asare [7] investigated the electrochemical behavior of pyrite in acid solution between -350 and +300 mV vs. SCE potential range, and found that peak potentials were independent of scan rate, however, the peak currents are proportional to scan rate. Conway et al [10] were investigated pyrite oxidation and proposed that

redox reactions were reversible between the potential ranges from -0.1 to 0.5 V at pH 1. They have drawn irreversible redox peaks above 0.5 V. In addition, pyrite voltammograms at higher pHs were also measured in this study, showing the increase in irreversibility at higher pHs. Authors connected this finding with the fact that in the neutral and alkaline solutions the state of S in the surface is more ionic than in the acid medium where disulfide species may be protonated in the interface.

In addition to the nature of the redox products formed at chalcopyrite surface, kinetics of these electrochemical reactions has also crucial importance since it directly determines the flotation performance. However, the kinetics of the electrochemical processes and the reversibility of the reactions have not been investigated in detail. Therefore, this research work was performed to investigate electrochemistry of chalcopyrite oxidation. CV tests were conducted in pH 4.67, pH 6.97, pH 9.2 and pH 11 buffer solutions at different scan rates.

MATERIALS AND METHODS

Highly mineralized chalcopyrite rock specimens (>98 % CuFeS₂) were obtained from Artvin-Murgul copper ore deposit of Black Sea Copper Works, Co., Turkey. Chemical analysis of the specimen was performed by atomic absorption spectroscopy, and surface analysis was conducted both by scanning electron microscopy and optic metal microscopy. These analysis techniques stated that major impurity was pyrite. Sample also contained sphalerite and quartz in trace amount.

Buffer solutions (Table 1) were used in order to prevent the changes that might occur in the pH of the solution as a result of the reactions that might take place between the mineral and the aqueous solution [11]. All the chemicals used for buffer preparation were in analytical grade. Dissolved oxygen in the solutions was removed by intensive bubbling of purified nitrogen (99.998%) for 15 minutes before each CV experiment. The flow of nitrogen was stopped during the experiment and the experimental set-up was completely sealed to prevent the diffusion of atmospheric oxygen into the cell.

Table 1. The composition of the buffer solutions

pH	Composition of the solution
4.67	0.5 M CH ₃ COOH + 0.5 M CH ₃ COONa
6.97	0.025 M KH ₂ PO ₄ + 0.025 M Na ₂ HPO ₄
9.20	0.05 M Na ₂ B ₄ O ₇
11.00	0.025 M NaHCO ₃ + 0.023 M NaOH

The CV experiments were performed in a conventional three-electrode system electrochemical cell in which a saturated calomel electrode, a platinum plate electrode with 1 cm² area and a mineral electrode were used as reference, counter and working electrodes, respectively. Although standard calomel electrode was used as the reference electrode, all the potentials reported in this paper have been converted to the standard hydrogen electrode (SHE) scale by adding 245 mV. The CV

experiments were performed using Bank Elektronik Wenking PGS95 potentiostat/galvanostat equipped with Zyklo computer program.

The chalcopyrite-working electrode was prepared from a massive specimen having a rectangular cross-section of 0.46×0.51 cm². Chalcopyrite specimen was mounted in a glass tube with an electrochemically inactive epoxy resin. Electrical connection was made internally by means of a Cu-wire and Hg. The surface of the chalcopyrite electrode was polished wet using 800-grit silicon carbide paper and then 1 μ m diamond paste before each run. After polishing the surface, the electrode was rinsed with distilled water and quickly transferred to the cell. On the other hand, the platinum electrode was cleaned using dilute chromic acid solution.

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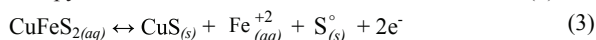
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RESULTS AND DISCUSSION

Redox Behavior of Chalcopyrite at pH 4.67

The cyclic voltammogram of chalcopyrite obtained in pH 4.67 buffer solution is given in Figure 1.a. Two easily observable peaks were obtained: one of them was in anodic region (A1), and the other one was in cathodic region (K1). Above 450 mV in the anodic region, a sharp increase in current density was observed indicating an anodic peak (A2), which caused formation of a small shoulder in the cathodic sweep. A small shoulder was also obtained around 350 mV in the anodic scan. To clarify this shoulder, a controlled sweep voltammogram (CSV) with different set points was measured (Figure 1.b) starting the scan from -100 mV in cathodic direction. Figure 1.b showed that this anodic shoulder could not clearly be defined as an anodic peak. As seen from CSV, when cycling proceeded, peak A1 formed in anodic scan, and in the reverse scan it resulted in peak K1. Peak A1 was attributed to the oxidation of chalcopyrite according to reaction (3) as proposed by Gardner and Woods [1]. This reversible reaction resulted in

the formation of K1, which corresponds to the reformation of chalcopryrite surface in the reverse direction of reaction (3).



In the following cycle of CSV returned from 450 mV (Figure 1.b), no additional peak appeared, but the current density of the cathodic peak K1 increased significantly. For a reversible process, size of the redox peaks is expected to be similar even at different anodic switching potentials. Hence, reaction (3) may not be fully reversible [10]. It has been established [12] that iron dissolves preferentially from chalcopryrite surface in acid solutions during oxidative leaching. Therefore, some part of the elemental sulfur was expected not be involved in the reformation of chalcopryrite but remained in the vicinity of the surface and presumably reduced to sulfide ions in the cathodic region proceeding the reaction (4) in the reverse direction.

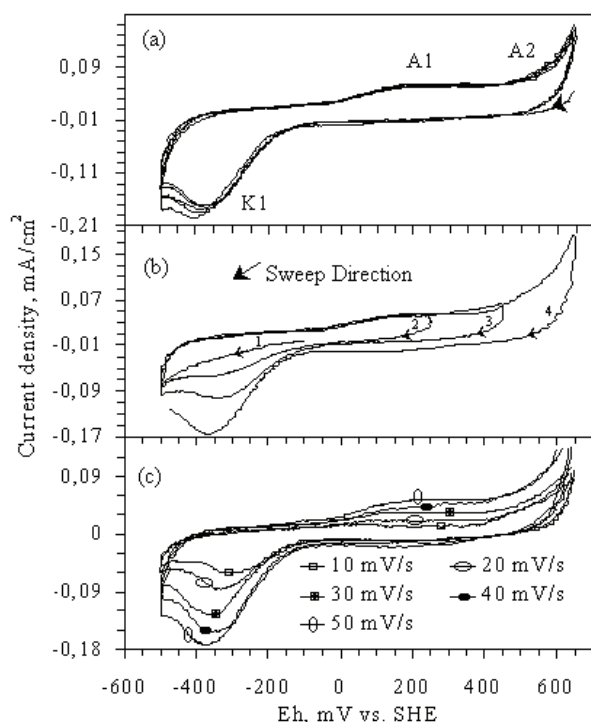
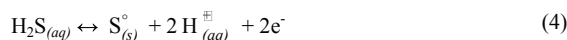
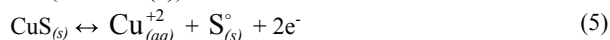


Figure 1. (a) Cyclic voltammogram of chalcopryrite ($v = 50$ mV/s), (b) controlled sweep voltammogram of chalcopryrite ($v = 50$ mV/s), (c) fifth cycles of chalcopryrite voltammograms measured at different scan rates (pH 9.2)

As the switching potential was increased to 650 mV, an additional anodic peak (A2) appeared showing oxidation of CuS (reaction (5)).



Peak A2 caused a shoulder around 150 mV in the cathodic scan indicating the reformation of CuS in minor amount (Figure 1.b). It also resulted in a substantial increase in the current density of peak K1, which was attributed to the increase in the amount of S° (reaction (5)). It was not involved in the reformation of CuS but rather reduced at lower potentials in the reverse direction of reaction (4). Although, thermodynamic considerations favor the formation of sulfate rather than elemental sulfur at high Eh values, the rate of oxidation of sulfides to sulfate is known to be

very slow and therefore, S° can exist as a metastable phase even in alkaline solutions [13].

As stated above, formation potential of a reversible redox reaction does not change by changing the scan rate in a CV study. However, its current density increases linearly with the square root of scan rate. Therefore, the data obtained at different scan rates is used in the examination of the reversibility of a redox reaction. Voltammograms of chalcopryrite were obtained at five different scan rates (10, 20, 30, 40 and 50 mV/s) in pH 4.67 buffer solutions. The last cycles (5th cycles) of these voltammograms are shown in Figure 1.c. There was a small shift in the peak position of A1 to oxidizing potentials at higher scan rates, whereas that of peak K1 was shifted to lower values. The change in the peak position with scan rate may be evaluated as an indicator for an irreversible process at a certain degree.

For a clear interpretation of the reversibility status of the redox processes, the current density of the major anodic (A1) and the cathodic (K1) peaks was plotted as a function of square root of the scan rate as illustrated in Figure 2. There was a linear relationship for both peaks. However, the lines did not go through the origin, which may be due to diffusion-controlled processes [6, 10]. Similar findings have been reported by Hemmingsen [14] in a voltammetric investigation performed on platinum, and explained by presence of additional peaks and traces of oxygen in the solution.

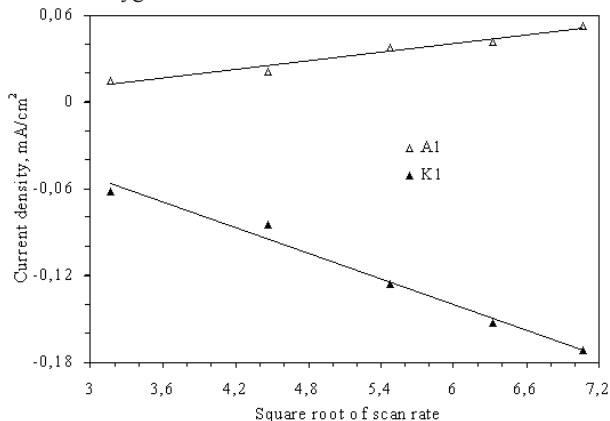


Figure 2. Relationship between current density of peaks and square-root of scan rate at pH 4.67

The linear relationship between the current density and square-root of the scan rate may be evaluated as an indicator for reversible redox processes. But, the large peak separation, the difference between the sizes of A1 and K1 and the shift in the positions of the redox peaks revealed that the redox processes occurring on chalcopryrite electrode surface in the scan range of -500 mV $+650$ mV and in slightly acidic solution could not be fully reversible. In addition, as stated above, all the products would not be reduced reversibly. Some of the elemental sulfur may be consumed in reformation of CuS (reaction (5)) and the rest reduced to H_2S .

Redox Behavior of Chalcopryrite at pH 6.97

Figure 3.a shows the chalcopryrite voltammogram obtained in pH 6.97 buffer solution at 50 mV/s scan rate between $+650$ mV and -500 mV. Three anodic and four cathodic peaks were observed. At the same scan rate, a controlled sweep

voltammogram was also measured (Figure 3.b) to better define the anodic oxidation peaks, which resulted in certain reduction peaks in the cathodic region.

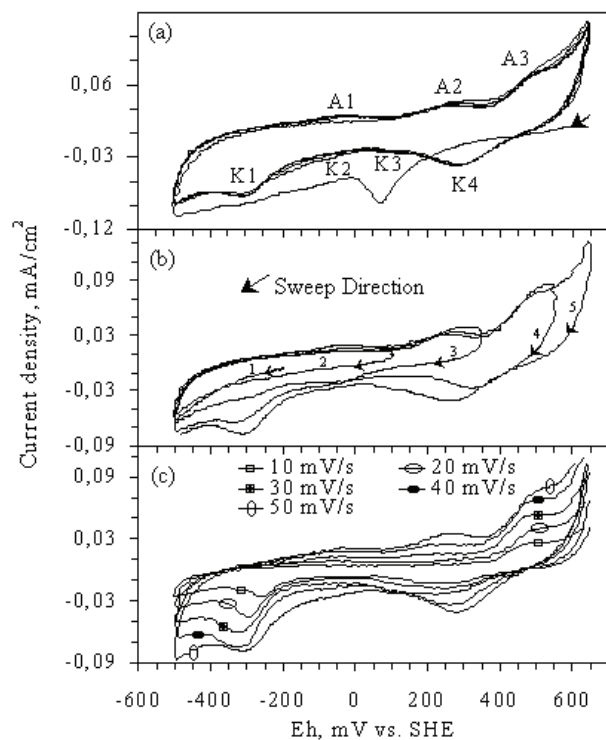
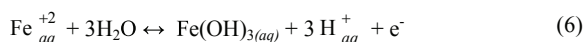


Figure 3. (a) Cyclic voltammogram of chalcopyrite ($v = 50$ mV/s), (b) controlled sweep voltammogram of chalcopyrite ($v = 50$ mV/s), (c) fifth cycles of chalcopyrite voltammograms measured at different scan rates (pH 9.2)

A sharp cathodic peak (peak K3) was formed in the first cycle of the chalcopyrite voltammogram (Figure 3.a), which shows the reduction of surface oxides formed during cleaning of the chalcopyrite electrode surface in the reverse direction of reaction (6). This peak appeared as a small shoulder in the following cycles. The CSV given in Figure 3.b shows that the peak K3 could only form as a small shoulder when the anodic switching potential was increased to 600 mV in the last cycle.



As mentioned in the experimental section, the mineral electrode surface was polished and then washed with distilled water before immersing it into deoxygenated buffer solution. Hence, electrode surface oxidation possibly occurred during washing after polishing; since, such a sharp peak appeared in the first cycle but not in the following cycles. However, there is a shoulder around 100 mV indicating that reaction (6) continues in minor scale in the following cycles. Similar reduction peak was also obtained on pyrrhotite surface and the same reduction reaction was referred [15]. This reaction initiates at 60 mV and 174 mV for 10^{-4} M Fe^{+2} and 10^{-6} M Fe^{+2} concentrations at pH 6.97, respectively [16].

Redox peak formation did not clearly observe in the first cycle of the CSV (Figure 3.b). However, when the switching potential was increased to 350 mV in anodic region, one anodic peak (A2) and two cathodic peaks (K1 and K2) formed. The peak A2 was not considered as fully reversible, since it does not

only form the cathodic peak K2, but also contributes to increase the current density of K1 in the cathodic scan. Moreover, the size of K2 is smaller than A2. On the cyclic voltammogram given in Figure 3.a, the peak K2 formed as a small shoulder, but the peaks A2 and K1 have large current densities. These findings support the conclusion that the redox reaction caused formation of A2 was not fully reversible.

The anodic peak (A2) shows possibly the oxidation of chalcopyrite surface according to reaction (7), and K2 corresponds to reduction of oxidation products in the cathodic scan [1]. As stated above, reaction (7) is not considered fully reversible since formation of A2 was resulted in formation of K2 and also a significant increase in the current density of K1, which may correspond to reduction of elemental sulfur (Figure 3.b). At the end of this reduction process, both H_2S (reaction (4)) and/or HS^{-} (reaction (8)) may form, since the solution pH was very close to the stability limit of $\text{H}_2\text{S}/\text{HS}^{-}$ at pH 7 [16]. Reactions (4) and (8) are expected to occur at -93 mV and -89 mV in the cathodic region for 10^{-6} M H_2S and 10^{-6} M HS^{-} , respectively.

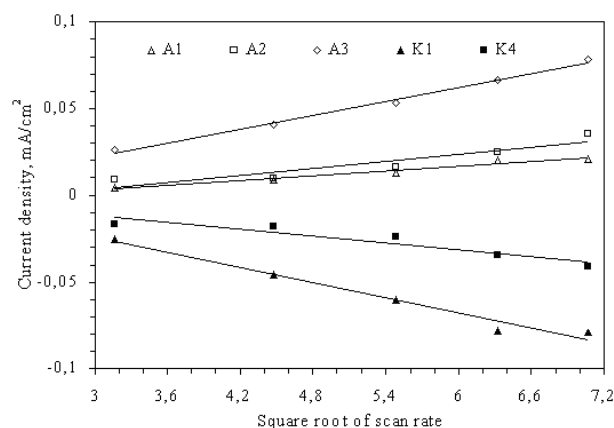
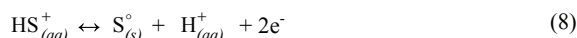
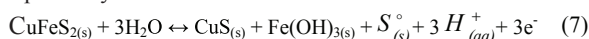
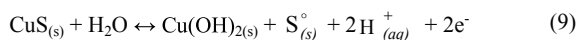


Figure 4. Relationship between current density of peaks and square-root of scan rate at pH 6.97

Cycling the potential from 550 mV in the anodic region resulted in formation of three new peaks: A1 and A3 in the anodic region and K4 in the cathodic region. Oxidation of H_2S (reaction (4)) and/or HS^{-} (reaction (8)) would give rise to peak A1 and form elemental sulfur. On the other hand, as proposed by Gardner and Woods [1], the peak A3 shows oxidation of CuS , a reaction product of chalcopyrite oxidation (reaction (7)), according to reaction (9). This reaction starts to occur at 450 mV at pH 6.97.



The peak K4 would show the reformation of CuS , which prove the reversibility of reaction (9). However, this redox reaction may not be fully reversible, since it also contributed to increase the current density of peak K1. Moreover, the shift in maximum current density point of peak K4 to more reducing potentials in the last cycle of CSV may be an indicator of slow electron transfer.

Voltammograms of chalcopryrite were also obtained at different scan rates in pH 6.97 buffer solution (Figure 3.c). Positions of the anodic peaks did not change significantly and there was only a small shift in the peak position of K1 to more reducing potentials, which indicate the irreversibility to some extent. Figure 4 was also plotted to elucidate the relationship between the current density and square root of the scan rate for the anodic and the cathodic peaks appeared in pH 6.97 (Figure 3.b). Linear relationship was observed between the current density and the square root of the scan rate for all the peaks. However, the lines did not exactly extrapolate through zero indicating the diffusion-controlled processes. For a reversible process, same peak potential, and linear relationship between current density and square root of sweep rate would not be enough. Additionally, peak separation should also be small, and sizes of reduction and oxidation peaks should be equal [4-5]. Therefore, the redox reactions occurring between 650 mV and -500 mV at pH 6.97 were not fully reversible. Further, all of the oxidized products were not reduced in the cathodic scan (Figure 3.b).

Redox Behavior of Chalcopryrite at pH 9.2

A cyclic voltammogram was drawn to elucidate the redox behavior of chalcopryrite in pH 9.2, tetraborate buffer solution (Figure 5.a). Only one anodic (A1) and one cathodic (K1) peaks were obtained. A CSV was also measured to establish the reversibility of the redox reactions (Figure 5.b). There was no peak formation in the first cycle switched from 50 mV. When the switching potential was increased to 400 mV formation of an anodic peak (A1) and a cathodic peak (K1) was observed. The peak A1 corresponds to chalcopryrite oxidation by reaction (7). The oxidation products were reduced during the cathodic scan in the reverse direction of reaction (7), which resulted in formation of K1.

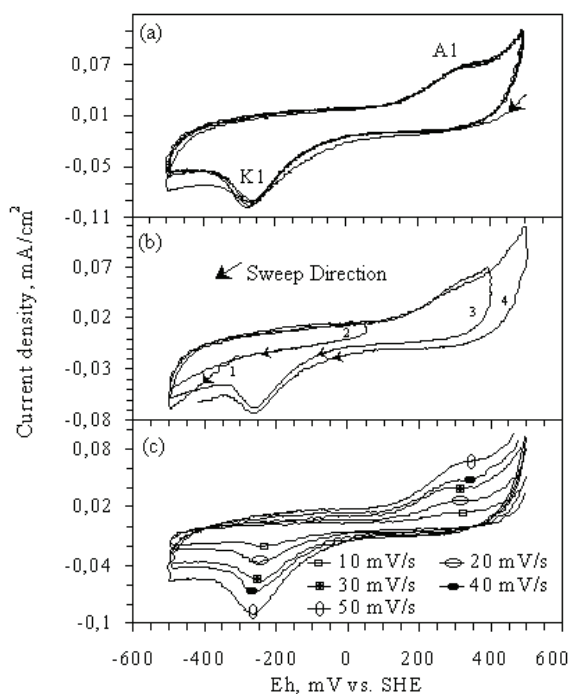


Figure 5. (a) Cyclic voltammogram of chalcopryrite ($v = 50$ mV/s), (b) controlled sweep voltammogram of chalcopryrite ($v = 50$ mV/s), (c) fifth cycles of chalcopryrite voltammograms measured at different scan rates (pH 9.2)

The cyclic voltammograms were also obtained at different scan rates (Figure 5.c) to evaluate the reversibility of the redox process observed between +500 mV and -500 mV potential range. The same peaks were also observed at lower scan rates but with lower current density. There was a slight shift in the peak potential of K1 towards reducing potentials. This was attributed to slow electron transfer [4-6]. In addition, the relationship between the current density and square root of the scan rate was linear for both peaks, which may be assessed as a reversible process (Figure 6). However, large separation between peaks A1 and K1 shows that redox processes would not be fully reversible.

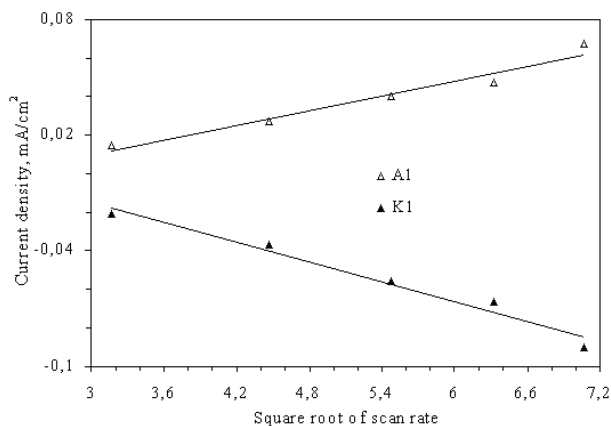


Figure 6. Relationship between current density of peaks and square-root of scan rate at pH 9.2

Redox Behavior of Chalcopryrite at pH 11

Electrochemical behavior of chalcopryrite was investigated between +500 mV and -500 mV potential range at 50 mV/s sweep rate in strongly alkaline pH (Figure 7.a). A1 in the anodic region and, K1 and K2 in the cathodic region came into view at pH 11. A CSV was also measured at the same scan rate to clarify the redox reactions corresponding to the anodic and the cathodic peaks (Figure 7.b). The potential was cycled from 0 mV, 300 mV and 500 mV in the anodic region. There was no peak formation in the first cycle. However, in the second cycle, the peak A1 formed in the anodic scan and resulted in formation of K1 in the reverse scan. The anodic peak (A1) corresponds to the oxidation of chalcopryrite (reaction (7)). In the reverse scan, the peak K1 shows presumably reformation of chalcopryrite in the reverse direction of reaction (7).

In the last cycle of CSV, there was a sharp increase in the current density above 300 mV, and this anodic process resulted in the formation of small peak (K2) in cathodic region. This new anodic peak was considered to be responsible for oxidation of CuS, a product of chalcopryrite oxidation, according to reaction (9). This reaction is not fully reversible because of large separation between the two peaks. In addition, formation of a small cathodic peak (K2) in the negative-going scan shows that the reaction (7) was not fully reversible, and some of the oxidation products might exist on the surface as more stable and irreversible compounds. Figure 7.c shows the 5th cycles of the chalcopryrite voltammograms measured at different scan rates for a clear interpretation of redox behavior of chalcopryrite at pH 11. Formation potentials of the anodic peaks shifted to

more oxidizing potentials at higher scan rates, whereas those of the cathodic peaks did almost not change. Slow electron transfer and/or changes in the composition of the passive layer on chalcopryrite may result in larger peak separation at higher scan rates.

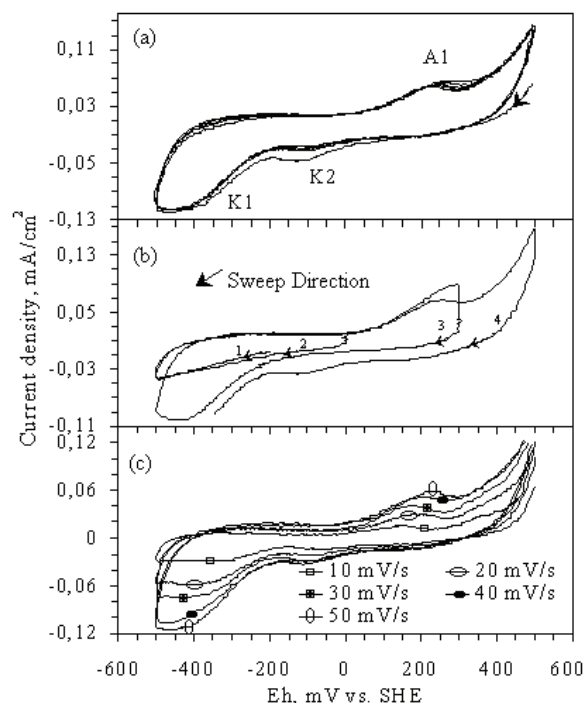


Figure 7. (a) Cyclic voltammogram of chalcopryrite ($v = 50$ mV/s), (b) controlled sweep voltammogram of chalcopryrite ($v = 50$ mV/s), (c) fifth cycles of chalcopryrite voltammograms measured at different scan rates (pH 9.2)

Figure 8 shows the relationship between the current density and square root of the scan rate for the peaks A1, K1 and K2 at pH 11. The linear relationship in Figure 8 is an indication of the reversibility of the reactions. But, larger peak separation between the anodic and the cathodic peaks, deviation in lines of current density vs. square root of scan rate from origin, and differences between the sizes of peaks indicated that redox reactions may not be full reversible.

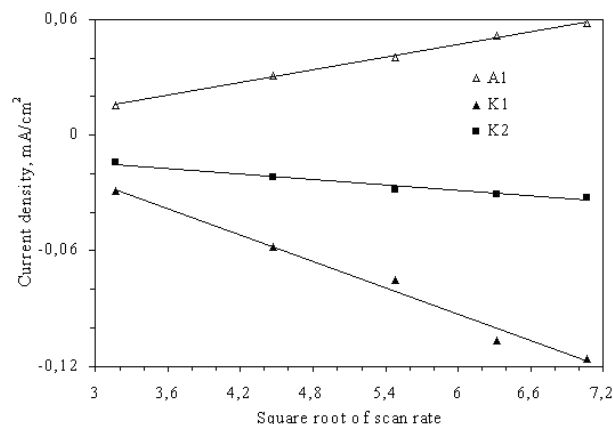


Figure 8. Relationship between current density of peaks and square-root of scan rate at pH 11

CONCLUSIONS

Electrochemistry of chalcopryrite oxidation was studied at four different pHs by using cyclic voltammetry technique at different switching potentials and scan rates. Therefore, reversibility and kinetics of the redox reactions occurring on chalcopryrite surface were investigated in detail.

The cyclic voltammograms suggested that chalcopryrite oxidation-reduction process was not fully reversible possibly due to irreversible surface coverage by iron-hydroxides and/or diffusion of metal ions into solution. Reduction of oxidized products into different chemical forms, differences between sizes of oxidation and reduction peaks, shift in the formation potential of redox reactions, diffusion-controlled processes, and large separation between redox peaks are indicators for the irreversibility of the oxidation products of chalcopryrite at certain degree. At least one of these deviations was observed at all pH values tested but with varying degree. The most complicated electrochemical behavior of chalcopryrite was observed in neutral solution. However, the reactions at alkaline pH values were quite clear and have higher degree of reversibility.

The electrochemical reactions at pH 4.67 were not fully reversible probably due to diffusion of ferrous ions dissolved from chalcopryrite during the anodic scan. Therefore, reformation of chalcopryrite in the cathodic scan was failed and the elemental sulfur remained in the vicinity of the electrode surface was mostly reduced to H_2S form.

Anodic oxidation of chalcopryrite in neutral solution (pH 6.97) resulted in formation of copper sulfide, iron hydroxide as well as elemental sulfur. However, very small amount of elemental sulfur was involved with reformation of chalcopryrite in the cathodic scan, which led to formation of irreversible redox reactions. Most of the elemental sulfur was reduced to H_2S/HS^- form at strongly reducing environment. The difference in the kinetics of the anodic and the cathodic reactions was considered as the main reason for this kind of irreversibility.

The electrochemical reactions observed at alkaline solutions (pH 9.2 and 11) were seemed to be almost reversible, but they were not fully. Formation of copper sulfide, iron hydroxide and elemental sulfur was proposed depending on the electrode potential. However, most of the elemental sulfur formed during anodic oxidation was involved in reformation of chalcopryrite surface since reduction potential of elemental sulfur to HS^- form in alkaline solutions is very low and out of the scanning range applied in this study.

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