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# Electrochemical behavior of pyrite in sulfuric acid solutions containing silver ions

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A systematic electrochemical study of pyrite in $H_2SO_4$ solutions containing dissolved silver was undertaken to gain more information about the transfer of silver ions to pyrite and their role in enhancing the direct oxidation of pyrite. The results of cyclic voltammetry experiments provide additional evidence of the formation of metallic silver on the $FeS_2$ surface under open-circuit conditions. A pyrite electrode held at the open-circuit potential for 2 h in the presence of $10^{-3}$ M $Ag^+$ exhibits a large and sharp anodic peak at about 0.7 V. The current associated with this peak is the result of the dissolution of metallic silver deposited during the initial conditioning period. There is no evidence of silver deposition without preconditioning until the potential drops below about 0.6 V for $Ag^+$ concentrations ranging from $10^{-4}$ to $10^{-2}$ M. However, subsequent silver deposition appears to be very sensitive to the dissolved silver concentration in this range. There is also evidence that the state of the pyrite surface has a pronounced influence on its interaction with silver ions. Agitation has also been found to have a significant effect on the electrochemistry of the Ag–$FeS_2$ system.

## 1. Introduction

Pyrite is the most common of the sulfide minerals and is found in a variety of geological settings. As one of the most widely occurring minerals, pyrite is a prevalent host for gold in precious metal deposits. However, the gold is often finely disseminated in the pyrite matrix and not amenable to extraction by conventional cyanidation. The pretreatment of pyritic ores and concentrates prior to cyanidation has in some instances improved gold recovery. Several pretreatment approaches have utilized oxidative leaching processes, involving both pressure oxidation [1, 2] and bio-oxidation [3, 4]. However, these techniques result in the production of large quantities of sulfate which must be rejected from the system in an environmentally acceptable form.

It is possible to control the aqueous oxidation of pyrite so as to yield elemental sulfur as the principal sulfur reaction product. The elemental sulfur product typically forms a dense, tenacious, protective and insulating coating on the pyrite particles. Though environmentally safe, a sulfur coating can limit the rate of pyrite oxidation. Chalcopyrite dissolution under similar conditions is also limited by the presence of elemental sulfur. Some researchers have attributed the extremely slow kinetics of ferric sulfate leaching of chalcopyrite to the difficulty of transport of electrons through the insulating elemental sulfur layer [5].

It has been shown for chalcopyrite that small additions of silver ions can enhance the leaching of copper [6–8]. Miller and Portillo [8] have investigated the mechanistic details of the enhancing influence of silver ion addition on the ferric sulfate leaching of chalcopyrite. They propose that $Ag^+$ reacts rapidly with $CuFeS_2$ to form a thin layer of $Ag_2S$ on the chalcopyrite surface as follows:

$$CuFeS_2 + 4Ag^+ = 2Ag_2S + Cu^{2+} + Fe^{2+} \quad (1)$$

The $Ag^+$ is then regenerated by the oxidation of $Ag_2S$ with ferric ion

$$2Fe^{3+} + Ag_2S = 2Fe^{2+} + 2Ag^+ + S^0 \quad (2)$$

The overall reaction results in the formation of a porous, nonprotective elemental sulfur layer instead of the otherwise protective layer, thereby increasing the rate of chalcopyrite leaching. Furthermore, it has been suggested that the formation of $Ag_2S$ at the $CuFeS_2$ surface significantly improves the conduction properties of the elemental sulfur. Wan *et al.* [9] have recently shown that the initial reaction rate for the leaching of chalcopyrite/carbon aggregates is approximately 3–4 times faster than that for chalcopyrite alone, suggesting that the increased electronic conductivity of the sulfur layer increases the rate of leaching.

In an attempt to more completely understand the interactions between $Ag^+$, $Ag_2S$, $CuFeS_2$ and the $Fe^{3+}/Fe^{2+}$ couple, Price and co-workers [10, 11] investigated the electrochemical behavior of $Ag_2S$ and $CuFeS_2$ electrodes under various conditions. Careful analysis of cyclic voltammetry data for the $CuFeS_2$ electrode in the presence of silver ions revealed that metallic silver in addition to $Ag_2S$ forms on the chalcopyrite surface. Cyclic voltammograms revealed that

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for a $CuFeS_2$ electrode immersed in a 1.0 M $H_2SO_4$ and $10^{-2}$ M $Ag^+$ solution, anodic scans yield a silver dissolution peak at about 0.7 V SHE and that the size of the peak is very dependent on length of the immersion time.

The effect of additions of silver ions on the direct oxidation of pyrite has been the subject of a recent investigation [12]. The rate of silver transfer to the pyrite surface is considerably slower and exhibits a higher activation energy than that for chalcopyrite. Detailed X-ray photoelectron spectroscopy (XPS) analysis of reacted pyrite particles indicates that elemental silver and elemental sulfur are the primary surface species formed by this interaction, and that only minor amounts of $Ag_2S$ are produced. The proposed reaction for silver transfer to the pyrite surface proceeds according to

$$2Ag^+ + FeS_2 = Fe^{2+} + 2S^0 + 2Ag^0 \quad (3)$$

The reduction of $Ag^+$ at the $FeS_2$ surface is similar to an electrochemical cementation reaction where a more noble metal is precipitated by a more electropositive metal. The purpose of the present study is to gain more information for the Ag–$FeS_2$ system, using standard electrochemical techniques. Cyclic voltammetry experiments have been performed to study the behavior of a $FeS_2$ electrode in $H_2SO_4$ solutions containing various additions of $Ag^+$. The effects of silver concentration, conditioning time and stirring have been investigated.

## 2. Experimental details

The high purity pyrite used in this investigation was obtained in the form of massive crystals from Zacatecas, Mexico. Chemical analyses for this sample which have been repored elsewhere [12] reveal that, on the average, it contains 44.5% Fe and 52.9% S. The pyrite electrode was prepared by cutting a cube (~ 1 cm) from the massive mineral specimen and casting it in an epoxy resin with the working face exposed by grinding and polishing. A small hole was drilled through the back of the electrode holder, penetrating several mm into the pyrite. A glass tube was attached to the holder and secured with epoxy cement. Electrical contact was established by placing a small amount of mercury in the tube and inserting a copper wire.

A fresh surface was produced on the electrode prior to each experiment by hand polishing successively with 240–600 grit silicon carbide papers. After rinsing thoroughly with distilled water, the electrode was immediately immersed in the electrolyte. All solutions were prepared with reagent grade chemicals and distilled deionized water.

An EG & G Princeton Applied Research Model 273 potentiostat/galvanostat was used for the voltammetric studies. A Houston Instrument Model 200 *XY* Recorder was used to trace the voltammograms. Experiments were performed in a 1-l cell which is shown schematically in Fig. 1. Electrochemical measurements were carried out at room temperature (~ 23° C) in solutions deoxygenated with nitrogen. To avoid chloride leakage from a saturated calomel reference electrode and possible precipitation of silver chloride in the electrolyte, a mercury–mercurous sulfate reference electrode was used for all experiments. The standard potential for the Hg–$Hg_2SO_4$ reference electrode is 0.614 V versus the standard hydrogen electrode (SHE). All potential values in this paper are reported with respect to the SHE.

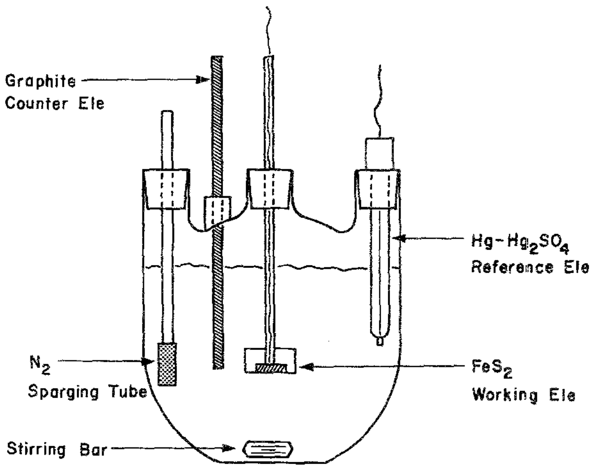

Fig. 1. A schematic representation of the electrochemical cell arrangement used in this investigation.

## 3. Results and discussion

### 3.1. *$FeS_2$ in the absence of $Ag^+$*

The electrochemical behavior of $FeS_2$ in sulfuric acid solutions has been investigated using cyclic voltammetry by various researchers [13–16]. In general, there has been good agreement between the different studies. Biegler and Swift [13] and Meyer [14] examined the anodic polarization of $FeS_2$ at 25° C in deoxygenated solutions using 1.0 M and 1.5 M $H_2SO_4$ respectively. The initial rest potential for freshly prepared pyrite surfaces ranged from 0.55 to 0.65 V vs SHE. Very low currents were measured between the rest potential and about 0.9 V at which point there was a sharp rise in current. The anodic wave shifts to more negative potentials with increasing pH.

Figure 2 shows the cyclic voltammograms obtained with a polished $FeS_2$ electrode in 0.25 M $H_2SO_4$ scanned to different anodic limits. Each scan originated at the rest potential (0.60 V vs SHE) and proceeded in the anodic direction. The curve represented by the dashed line was obtained using an anodic limit of 0.82 V and shows very little oxidation reaction taking place. Using 1.07 V as the anodic limit, the solid curve exhibits an exponential current increase starting at about 0.9 V. The scan shows the typical hysteresis (higher anodic currents after reversal) found with pyrite. The curves cross at about 0.93 V which is in accordance with the results of other investigators.

Although the degree of definition in the curves shown in Fig. 2 is rather low the general appearance is similar to that reported by Biegler [16] for the poten-

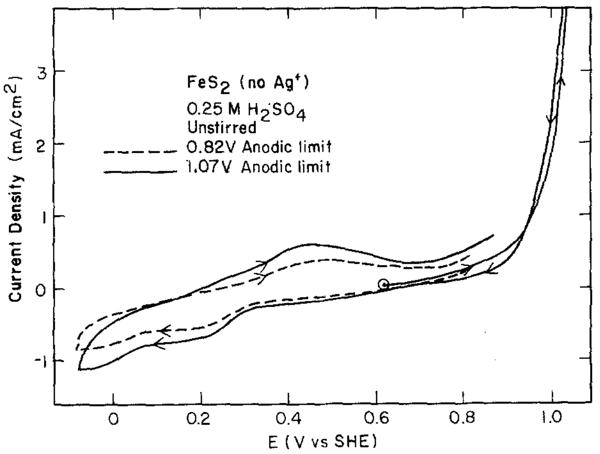

Fig. 2. Cyclic voltammograms for a pyrite electrode in 0.25 M $H_2SO_4$ without silver ions scanned to different anodic limits.

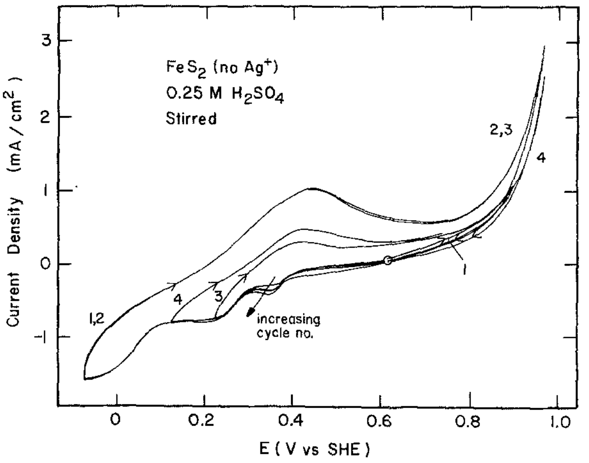

Fig. 3. Cyclic voltammograms for a pyrite electrode in 0.25 M $H_2SO_4$ without silver ions scanned to different cathodic limits.

tial region between 0.60 to −0.16 V vs SHE. As proposed by Biegler, the cathodic peak at 0.25 V probably arises from the reduction of pyrite according to the following reaction:

$$FeS_2 + 2xH^+ + 2xe \longrightarrow FeS_{2-x} + xH_2S \quad (4)$$

When the scan is reversed back in the anodic direction, a broad anodic peak at about 0.4 V appears. It is not likely that this peak involves the oxidation of element sulfur that may have been generated during the previous scan for two reasons. Firstly, the peak appears whether or not the upper limit during the previous anodic scan is high enough for any oxidation to occur. Secondly, most of the pyrite oxidation takes place at potentials above 0.9 V and, based on the work of Bailey and Peters [17] and Peters and Majima [18], the predominant reaction should be

$$FeS_2 + 8H_2O \longrightarrow Fe^{3+} + 2SO_4^{2-} + 16H^+ + 15e \quad (5)$$

Thus, not much elemental sulfur should be present on the pyrite surface even when oxidation is allowed to occur.

The more likely situation is that the anodic peak at 0.4 V involves the oxidation of a species generated during the cathodic scan. In order to test this hypothesis, the cyclic scan shown in Fig. 3 was performed. The scan began at the open-circuit potential and preceeded up to an anodic limit of 0.92 V, before being reversed down to −0.08 V in the first cycle. In the subsequent cycles, the upper limit was increased to 0.97 V and maintained at this level thereafter, while the cathodic limit was successively changed from −0.08 to 0.22 to 0.12 V.

The results show that the current due to pyrite oxidation increases on going from cycle 1 to cycle 2 because the anodic limit is raised. However, at the same time, the anodic peaks at 0.4 V which follow afterward in the scans remain unchanged. They show a difference in size in cycles 3 and 4 only after the cathodic limit has been changed. In fact, the more positive the lower limit is (and hence lower the amount of reduction), the smaller the anodic peak at 0.4 V becomes. This sensitivity to the cathodic limit, but not the anodic limit, provides convincing evidence that it is one or more of the reduction products of reaction 4 that is being oxidized. Furthermore, it is not likely that $H_2S$ is involved since the anodic peak appears and the behavior shown in Fig. 3 is the same regardless of whether or not the electrolyte is being stirred. Based on these considerations, we can attribute the peak at 0.4 V to the oxidation of the non-stoichiometric pyrite, $FeS_{2-x}$.

### 3.2. *$FeS_2$ in the presence of $Ag^+$*

Our previous work [12] indicated that silver ions react with pyrite to primarily form metallic silver although a small amount of $Ag_2S$ may also be formed. The electrochemical response of silver sulfide in sulfuric acid solutions was studied by Price *et al.* [11]. Beginning the scan from the rest potential, the voltammogram exhibited an increase in anodic current up to approximately 1.2 V. The anodic reaction in this potential region was attributed to

$$Ag_2S = 2Ag^+ + S^0 + 2e \quad (6)$$

During the cathodic scan, metallic silver was formed at the electrode not only from the reduction of dissolved silver (0.50–0.55 V) but also from the direct reduction of $Ag_2S$ (−0.12 V). Subsequently, the oxidation of metallic Ag produced a large and distinctive anodic peak at 0.70 V.

Based on the electrochemical behavior of $Ag_2S$ and of pyrite in the absence of $Ag^+$, it is obvious that to electrochemically differentiate the anodic oxidation of $Ag_2S$ from that of $FeS_2$ would be very difficult. However, the peak associated with the anodic dissolution of metallic Ag can serve as a useful fingerprint to study the system. The cyclic voltammogram in Fig. 4 shows the electrochemical behavior of $FeS_2$ in the presence of $10^{-3}$ M $Ag^+$. The electrode was held at the open-circuit potential for 2 h prior to initiating the anodic potential sweep. On the first cycle, the current rises almost immediately to form a large and sharp anodic

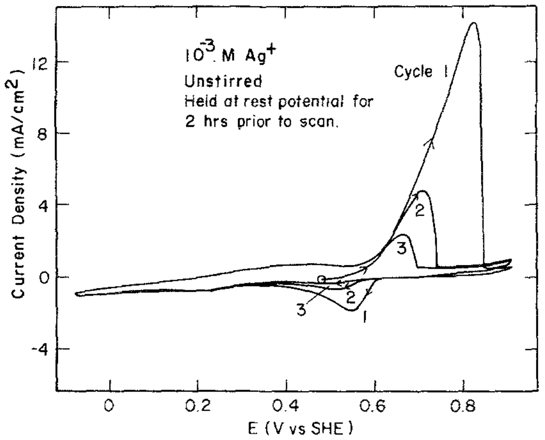

Fig. 4. Cyclic voltammograms for pyrite after being held for 2 h in the presence of $10^{-3}$ M $Ag^+$ and 0.25 M $H_2SO_4$ at open-circuit potential conditions.

peak. Price *et al.* [11] observed a similar peak at the same potential during their study of $Ag_2S$ and assigned it to the anodic dissolution of metallic Ag to $Ag^+$. The very steep increase in current and nearly vertical drop associated with the peak in Fig. 4 is also typical of metal dissolution processes [19, 20]. Furthermore, attributing the peak to silver dissolution confirms the finding in our previous investigation that metallic silver deposits onto pyrite under open-circuit conditions.

A continuation of the scan in the reverse direction reveals the onset of a cathodic peak at about 0.6 V. This potential is in excellent agreement with that predicted from the Nernst equation for the deposition of silver in a system containing $10^{-3}$ M $Ag^+$ (i.e. 0.62 V). Furthermore, it is close to the rest potential that we have measured when the pyrite electrode is first immersed in the electrolyte containing silver. It is also interesting to note that the open-circuit potential of pyrite alone in a silver-free solution has much the same value. The close proximity of these potentials is consistent with the observations from our earlier study on the $Ag^+/FeS_2$ system [12] that metallic silver begins to form on ground pyrite particles according to reaction 3 very rapidly after the sulfide is contacted with the electrolyte.

These results also indicate that iron oxide which is inevitably present on both ground and polished pyrite samples prior to immersion does not inhibit the subsequent reactions. In fact, it is most likely that the 0.25 M $H_2SO_4$ used in these experiments immediately dissolves the oxide from the surface.

### 3.3. *Effect of $Ag^+$ concentration*

In Fig. 5, the effect on the electrode response of the $Ag/FeS_2$ system of varying the $Ag^+$ concentration in the electrolyte from $10^{-4}$ to $10^{-2}$ M is represented. In each of the experiments, the scan was performed according to the following program: proceeding immediately from the open-circuit potential up to an anodic limit of 0.82 V at a speed of 20 mV $s^{-1}$, before being reversed cathodically down to a lower limit of −0.08 V and finally back in the anodic direction for a second time. An anodic limit of 0.82 V was chosen since this would be sufficiently high to permit the anodic dissolution of any deposited silver but not any of the underlying pyrite. As noted in the figure, the solution was left unstirred throughout these particular experiments.

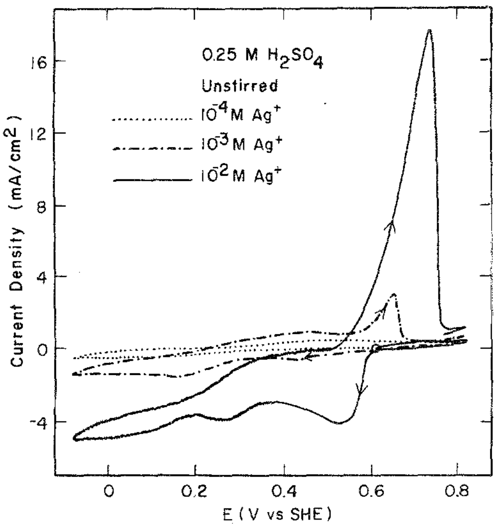

Fig. 5. Cyclic voltammograms for a pyrite electrode immersed in 0.25 M $H_2SO_4$ as a function of silver ion concentration. The scan commenced in the anodic direction from the open-circuit potential.

In the presence of $10^{-4}$ M $Ag^+$, there is no evidence that any silver deposition occurs during the cathodic scan and the voltammogram appears to be very similar to the one obtained in the absence of any dissolved silver. We can estimate that for about 1 min during the sweep the potential is in a range (from 0.6 V on the cathodic scan until 0.5 V on the second anodic-going scan, using the voltammogram in Fig. 5 as a guide) where deposition is possible. It turns out that in unstirred solutions containing $10^{-4}$ M $Ag^+$ the length of this exposure time is critical to whether any deposition can be detected. Our experiments have shown that a period of 10 min is not long enough, but that 2 h is.

A 10-fold increase in the silver level to $10^{-3}$ M does change the electrode response during the initial anodic scan to 0.82 V, but has a significant effect from that point onward. During the cathodic scan, more current flows than in the case of the lower silver concentration and two small current rises appear at approximately 0.43 and 0.16 V. When the sweep is reversed in the anodic direction for the second time, two current rises can again be seen. The first one, which begins at approximately 0.2 V, is the same as the one observed in the absence of silver (Figs 2 and 3), whereas the second one is due to the anodic dissolution of metallic silver. This suggests that two reactions have occurred during the cathodic scan: reduction of pyrite itself according to reaction 4 and silver deposition.

When the silver concentration is further increased to $10^{-2}$ M, the data indicate that a great deal more deposition now occurs. The apparent current density drops abruptly to approximately $-4$ mA $cm^{-2}$ at 0.6 V along the cathodic scan and remains at roughly this level until the lower potential limit is reached.

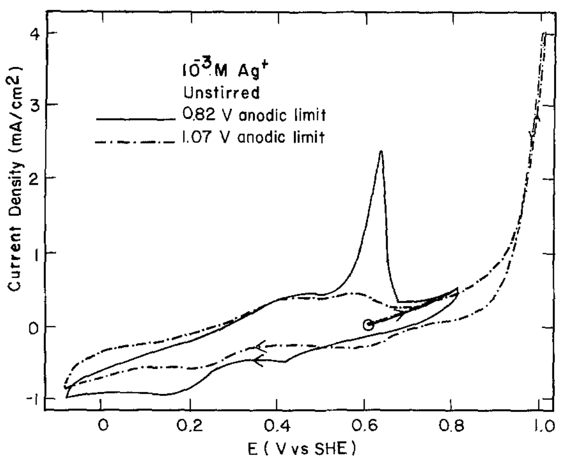

Fig. 6. Cyclic voltammograms for pyrite in the presence of $10^{-3}$ M $Ag^+$ and 0.25 M $H_2SO_4$ scanned to different anodic limits.

Thereafter, cathodic current continues to flow, albeit in a diminishing amount, as the scan proceeds in the anodic direction up to a potential of about 0.5 V, whereupon the anodic dissolution of the deposited metal begins. Another interesting observation concerning the voltammogram is that, from about 0.38 V on the negative-going portion of the cathodic scan until about 0.5 V on the positive-going part, tiny oscillations in the current signal are observed. This sort of noise is typical of the response in many deposition reactions [21–23].

### 3.4. *Effect of anodic limit*

An important aspect to investigate is the influence that the initial state of the pyrite surface has on its interaction with silver ions. To do this, a voltammogram obtained when the initial anodic scan is extended far enough for pyrite to be oxidized has been compared to one in which the mineral itself is not allowed to be oxidized. The results which are shown in Fig. 6 for a pyrite electrode immersed in a quiescent $10^{-3}$ M $Ag^+$ solution indicate that the history of the sample can be very important. When the upper potential limit is only 0.82 V, and no oxidation of pyrite itself can take place, it is evident from the appearance of the $Ag^0/Ag^+$ peak in the second anodic-going scan that silver deposition has occurred. In the second curve, in which the anodic limit has been extended to 1.07 V, very high current flows above approximately 0.9 V due to the oxidative dissolution of pyrite (compare with Fig. 2). This has a dramatic effect on the subsequent electrode response by reducing the current during the cathodic scan and almost entirely eliminating the $Ag^0/Ag^+$ anodic peak. It appears that surface products which form on the mineral during its oxidation passivate the pyrite surface and greatly inhibit the deposition of silver.

However, evidence from other experiments indicates that factors such as the $Ag^+$ concentration and the degree of agitation in the electrolyte have a large influence on how much pre-oxidation of the pyrite surface inhibits deposition. When a scan (not included in the paper) similar to the one above is performed in a solution containing $10^{-2}$ M $Ag^+$, a considerable amount of deposition still occurs after the potential has been raised to 1.07 V during the previous anodic scan and the mineral has been severely oxidized. Presumably, a higher anodic limit is required to suppress silver deposition under these circumstances. The effect of stirring will be discussed in the next section of this paper.

### 3.5. *Effect of agitation*

Since deposition reactions are typically controlled by mass transfer, it is important to look at the effect of agitation on the electrochemistry of the Ag-$FeS_2$ system. A previous experiment has indicated that if the scan begins immediately from the open-circuit potential, there is no evidence that any deposition occurs during the cathodic scan in the case of an unstirred solution containing $10^{-4}$ M $Ag^+$ (see Fig. 5). In order to create a situation more favorable for deposition, we immersed the electrode in a $10^{-4}$ M $Ag^+$ solution and then held it at a potential of 0.17 V for 10 min before beginning the scan in the anodic direction. The results obtained under both stirred and unstirred conditions are compared in Fig. 7. Since a potential of 0.17 V is well below the open-circuit potential, it is not surprising that cathodic current flows during the 10-min conditioning period in both cases. Considerable differences are observed, however, once the sweep begins. In a quiescent electrolyte, the anodic rise which begins at 0.2 V and is associated with the oxidation of the product of reaction 4 is much larger than that seen previously. The peak due to the dissolution of elemental silver still does not appear, however. When the solution is being stirred, on the other hand, both processes clearly occur during the anodic scan. Evidently, at a bulk concentration of $10^{-4}$ M $Ag^+$, the rate of silver deposition onto pyrite is strongly controlled by mass transfer effects and agitation is required for this reaction to compete with reaction 4 during cathodic polarization.

The effect of stirring on the electrode response in an electrolyte containing $10^{-3}$ M $Ag^+$ has also been investigated. For these experiments, the usual procedure of

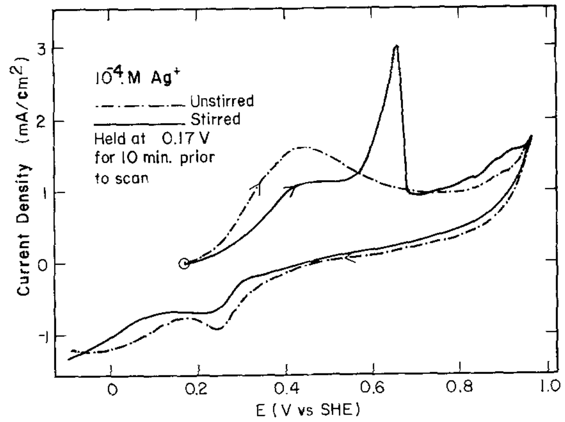

Fig. 7. The effect of stirring on the electrochemical response of pyrite in the presence of $10^{-4}$ M $Ag^+$ and 0.25 M $H_2SO_4$. The scan commenced in the anodic direction after the electrode potentials held at 0.17 V for 10 min.

beginning the sweep immediately from the open-circuit potential was adopted. In the case shown in Fig. 8, the anodic limit was increased to 1.07 V so that some oxidation of pyrite would occur before the cathodic portion of the scan began. (The voltammogram shown in this figure for quiescent conditions is the same as the one appearing in Fig. 6). As can be seen, stirring has a marked effect on the electrode response as soon as cathodic current begins to flow. The current signal becomes very noisy and remains so throughout the remainder of the cathodic scan. Such behavior is often observed in the case of mass transfer-controlled processes such as deposition, particularly when the hydrodynamic conditions are complex and not well controlled. It should be noted that a magnetic stirrer was used to agitate the solutions in this study and that this method should produce just such a complex flow pattern.

The biggest differences in the voltammograms arise after the potential reaches the cathodic limit and is again heading in the anodic direction. Under stirred conditions, the current remains negative and noisy all the way to a potential of about 0.5 V, whereupon it abruptly becomes positive and the large anodic peak due to the dissolution of elemental silver appears. The anodic rise which is associated with the oxidation of the product of reaction 4 is missing altogether. Agitation apparently enhances silver deposition enough in a solution containing $10^{-3}$ M $Ag^+$ that it becomes the dominant cathodic reaction.

Although the current signal becomes noisy during deposition when the solution is stirred, it does remain, on average, reasonably constant throughout the negative-going portion of the cathodic scan. Since this is the type of behavior expected for complete mass transfer control, it is interesting to compare the limiting current density for the conditions of this experiment with the level observed in the voltammograms. The limiting current density for silver deposition is given by:

$$i_l = \frac{-FD[Ag^+]}{\delta} \qquad (7)$$

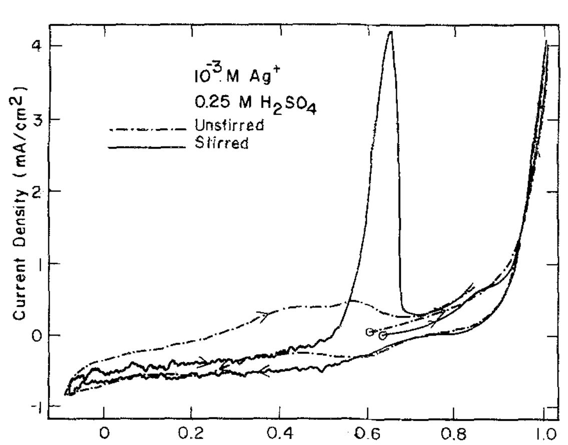

Fig. 8. The effect of stirring on the electrochemical response of pyrite in the presence of $10^{-3}$ M $Ag^+$ and 0.25 M $H_2SO_4$ when the pyrite surface is allowed to undergo oxidation prior to cathodic reduction.

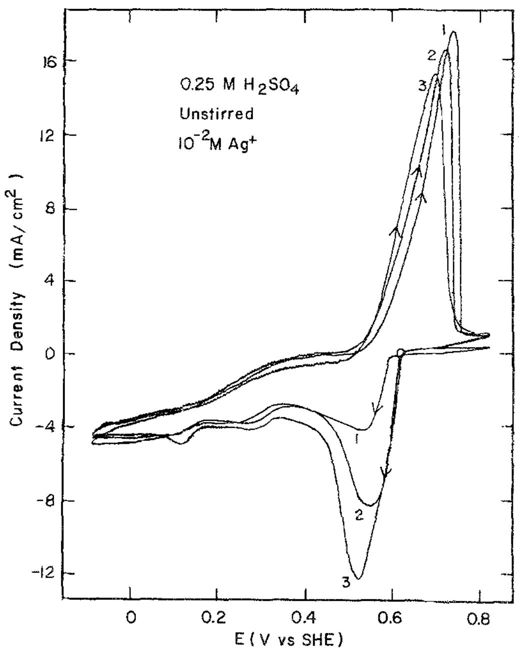

Fig. 9. Voltammograms showing the continuous cycling of the potential between −0.08 and 0.82 V for a pyrite electrode in the presence of a quiescent $10^{-2}$ M $Ag^+$ and 0.25 M $H_2SO_4$ solution.

where $\delta$, $F$, $D$ and $[Ag^+]$ are the boundary layer thickness, Faraday constant, diffusion coefficient and bulk $Ag^+$ concentration, respectively. Using the values $\delta = 5 \times 10^{-3}$ cm and $D = 1.6 \times 10^{-5}$ cm$^2$ s$^{-1}$ [24], we estimate the limiting current density in a solution of $10^{-3}$ M $Ag^+$ to be about −0.3 mA cm$^2$. Considering all the approximations that have been made, this is reasonably close to what is observed in Fig. 8.

It was observed in an earlier section that deposition can be inhibited if the upper limit during the previous anodic scan is too high. The results in Fig. 8 indicate that stirring tends to counteract this effect and that it can enable deposition to proceed even if some of the pyrite surface has been oxidized.

### 3.6. *Effect of continuous cycling*

Figure 9 shows the curves obtained after starting the scan from the open-circuit potential and then continuously cycling the potential between the limits −0.08 and 0.82 V. With each pass, more and more cathodic current flows and the first peak, in particular, becomes very prominant. It appears that by the end of the third cycle the electrode response during deposition has developed two distinct stages. The first is characterized by a large and relatively narrow peak located at about 0.5 V. Thereafter, the current drops quite sharply to more or less a plateau which marks the second stage. The reasonably constant current suggests that deposition is controlled by diffusion of $Ag^+$ ions to the pyrite surface during this second stage. The electrode signal is noisier during this phase and tiny oscillations in the current are observed throughout the remainder of the cathodic scan.

Analysis of the curves shows that the cathodic charge during each cycle is greater than the charge associated with the subsequent silver dissolution peak.

Furthermore, the difference seems to grow with each successive cycle. Assuming that deposition is the predominant reduction process, this means that some elemental silver still remains on the pyrite surface after each anodic scan and that the amount increases with each cycle. The presence of this silver may catalyze deposition in the succeeding cycle and in this way lead to the current increase that is observed.

It is important to keep in mind that the development of two stages in the electrode response has been observed during this study only when the electrolyte is left unstirred. Once agitation begins, the signal becomes extremely noisy and it becomes impossible to distinguish any clear pattern in the current–voltage behavior. Complex hydrodynamic conditions resulting from the use of a magnetic stirrer undoubtedly have a significant effect on this behavior.

## 4. Conclusions

The electrochemical behavior of pyrite in sulfuric acid solutions containing dissolved silver has been investigated to gain more information about the Ag–$FeS_2$ system. Cyclic voltammetry experiments were performed in an attempt to determine the silver products formed on the pyrite surface. Silver sulfide and elemental silver are two surface products that conceivably can result from the interaction between aqueous silver ions and pyrite. The electrochemical features associated with the oxidation of $Ag_2S$ overlap those of $FeS_2$ making it difficult to detect the presence of $Ag_2S$ by this technique. However, the peak assigned to the anodic dissolutions of metallic silver is very distinctive and can be used as a fingerprint to study the system. Furthermore, one would predict from thermodynamic data for the Ag–S–$H_2O$ system that Ag would be the primary reaction product and not $Ag_2S$. This was confirmed previously by detailed product characterization and analysis for the Ag–$FeS_2$ system [12].

The pyrite electrode when held at the open-circuit potential for extended times (2 h) in the presence of dissolved silver exhibits a large and sharp anodic peak at approximately 0.7 V which is attributed to the dissolution of metallic Ag to $Ag^+$. When scanning proceeds immediately from the open-circuit potential, there is no evidence of initial silver deposition for $Ag^+$ concentrations in the electrolyte ranging from $10^{-4}$ to $10^{-2}$ M. Cathodic currents due to silver deposition and the subsequent anodic currents for silver dissolution were very sensitive to the concentrations of dissolved silver. There is evidence that the state of the pyrite surface also has a pronounced influence on its interaction with silver ions. When the anodic limit is extended to potentials high enough to cause the oxidative dissolution of pyrite, surface products that form passivate the pyrite surface and greatly reduce the deposition of silver. However, other factors such as the $Ag^+$ concentration and the degree of agitation appear to influence the extent to which the preoxidation of pyrite inhibits deposition. For $10^{-3}$ M $Ag^+$, the voltammograms reveal that little silver deposition occurs under quiescent conditions when the anodic limit is set at 1.07 V, a point at which some $FeS_2$ oxidation occurs. On the other hand, there is considerable deposition of silver when the electrolyte is stirred.

Continuous cycling for unstirred conditions indicates that some elemental silver remains on the pyrite surface after each anodic scan and that the amount increases with each cycle. The presence of this silver appears to catalyze deposition in succeeding cycles.

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