SEMICONDUCTOR ELECTROCHEMISTRY COAL PYRITE

Technical Progress Report

October - December 1994

by

K. Osseo-Asare and Dawei Wei

Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

Prepared for the
United States Department of Energy

Under
Grant No. DE-FG22-91 PC 91303
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ABSTRACT

Pyrite dissolution in acidic solution was found to involve both electrochemical oxidation and chemical decomposition. The mechanism of chemical decomposition of pyrite in acidic solution may involve surface complexation of hydrogen ions. The anodic current of pyrite was relatively small in non-aqueous solution (acetonitrile) compared with that in aqueous solution. The implication is that the direct reaction of holes with $S_2^{2-}$ in the pyrite lattice was not significant and that the dissolution of pyrite required the presence of water. The anodic dissolution product was elemental sulfur which was detected by X-ray diffraction.

PROJECT OBJECTIVES

This project seeks to advance the fundamental understanding of the physico-chemical processes occurring at the pyrite/aqueous interface, in the context of coal cleaning, coal desulfurization, and acid mine drainage. A novel approach to the study of pyrite aqueous electrochemistry is proposed, based on the use of both synthetic and natural (i.e. coal-derived) pyrite specimens, and the utilization of pyrite both in the form of micro (i.e. colloidal and subcolloidal) and macro (i.e. rotating ring disk)-electrodes. Central to this research is the search for the relationships between the semiconductor properties of pyrite and the interfacial electrochemical behavior of this metal sulfide in aqueous systems. (Photo) electrochemical experiments will be conducted to unravel the mechanisms of anodic and cathodic processes such as those associated with pyrite decomposition and the reduction of oxidants such as molecular oxygen and the ferric ion.
STATEMENT OF WORK

The experiments to be conducted fall into two main groups, depending on whether the pyrite specimens are used in the form of (a) nanoparticle microelectrodes, or (b) planar surface macroelectrodes. In the first case, synthetic pyrite microelectrodes will be used in the form of nanoparticles and in the in-situ observation of the evolution of particle size and reaction products will be accomplished via photon correlation, absorption, and fluorescence spectroscopy techniques. In the second case, the experimental system will be based on a rotating ring disk electrode (RRDE) assembly, with coal pyrite serving as the disk and a Pt (or Ag, Cu) ring electrode permitting direct in-situ electroanalytical determination of reaction products.

DESCRIPTION OF TECHNICAL PROGRESS

INTRODUCTION

There have been numerous studies on pyrite dissolution in the literature (1-4). It is generally accepted that pyrite dissolution in acidic and oxidative conditions is an electrochemical process. This process can be described according to the following overall reactions (5-10):

\[
\text{FeS}_2 \rightarrow \text{Fe}^{2+} + 2\text{S}^0 + 2e^- \quad [1]
\]

\[
\text{FeS}_2 + 8\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 15e^- \quad [2]
\]

It is noted from Eq. [2] that oxidation of pyrite to sulfate involves 15 electron transfers for the overall reaction. Since electron transfer reactions are generally limited to one, or at
most two electrons, the overall reactions must involve several steps that require sulfur species of intermediate oxidation states.

Some of the investigators (9, 11) proposed that elemental sulfur formed initially as an intermediate species of pyrite oxidation (Eq. [1]), and was subsequently oxidized to sulfate. Another proposed mechanism for pyrite oxidation suggests that the formation of elemental sulfur and sulfate are independent processes. That is, the sulfur produced during the anodic dissolution of pyrite is a stable end product, but not an intermediate species in the sulfate reaction pathway (8). Other investigators have suggested that the end products of elemental sulfur and sulfate may be produced via intermediate sulfoxy anions, such as sulfite, SO₃²⁻, thiosulfate, S₂O₃²⁻, and polythionates, SₙO₆²⁻ (n = 4, 5, and 6) (10, 12, 13). Buckley and Woods (14) and Buckley et al. (15) postulated that instead of elemental sulfur, an iron deficient pyrite (Fe₁₋ₓS₂) was produced as a metastable product. Electrochemical experiments conducted by Mishra and Osseo-Asare (16, 17) showed that no significant anodic current was observed on pyrite electrode in a non-aqueous solvent. The authors concluded that reaction 1 does not take place as an elementary reaction during pyrite decomposition in aqueous solution. The reason elemental sulfur cannot be produced directly during pyrite decomposition was discussed on the basis of the solid-state chemistry of pyrite, and a hydroxide radical activation model was proposed (16, 17). However, direct evidence to show the presence or absence of elemental sulfur was not provided.

The presence of elemental sulfur on the pyrite surface is not only important for understanding the dissolution mechanism of the mineral, but also important for practical applications, such as mineral processing, hydrometallurgy, and acid mine drainage (AMD) control systems. The collectorless flotation of pyrite is attributed to the hydrophobicity of the elemental sulfur produced from a slight oxidation of pyrite (18, 19). From a hydrometallurgical extraction standpoint, the production of elemental sulfur from a metal
sulfide leaching process is preferred because elemental sulfur is directly marketable (4, 20). It is generally believed that a surface film of elemental sulfur on pyrite can hinder the mineral dissolution (1, 2, 11). Therefore, AMD prevention may be achieved by forming a passive film of elemental sulfur on the pyrite surface.

Direct detection of the dissolution products, especially for the intermediate species, is frequently difficult due to the inherent limitations of the specific analytical instruments, and the low stability and the small amount of the reaction products. Surface analysis by X-ray photoelectron spectroscopy (XPS) showed that the reaction products of pyrite dissolution involved species such as elemental sulfur (21, 22), polysulfides (21), and iron and sulfur oxides (22-25). Raman spectra collected by Mycroft et al. (21) and Zhu et al.(26) showed that both elemental sulfur and polysulfides formed on the surface of oxidized pyrite.

Elemental sulfur is kinetically stable at room temperature, although its oxidation should occur spontaneously from a thermodynamic point of view (8, 27). Hence, if elemental sulfur is an intermediate species, it should be detectable directly, provided enough reaction products can be obtained.

In this study, microelectrodes of pyrite were used to investigate the mechanism of pyrite dissolution. It was expected that the use of microelectrodes would provide more information on the dissolution mechanism of pyrite, by yielding stronger electrochemical responses and more reaction products. Electrochemical measurements and dissolution experiments were carried out to determine the contributions of electrochemical and chemical reactions in pyrite dissolution processes. Electrochemical measurements were performed in both aqueous and non-aqueous (acetonitrile) solutions to probe the pathways for the anodic dissolution of pyrite. Reaction products were analyzed directly using X-ray diffraction techniques.
EXPERIMENTAL PROCEDURES

Materials

Reagent grade ferric chloride (FeCl₃·6H₂O), sodium hydrosulfide (NaHS·xH₂O), nitric acid (HNO₃), sodium hydroxide (NaOH), and potassium nitrate (KNO₃) were obtained from Aldrich. Carbon disulfide (CS₂) from Aldrich contained 99.9% CS₂. Acetonitrile (99.5% CH₃CN) and tetra-n-butylammonium perchlorate, (C₄H₉)₄NClO₄) were purchased from Alfa. High purity water (18 MΩ-cm) was generated from a Millipore Milli-Q system. The water was deoxygenated by bubbling nitrogen. The nitrogen was prepurified by flowing the gas over a bed of copper filings at 450 °C to remove oxygen.

Pyrite Preparation

Synthetic pyrite particles were used as microelectrodes in the electrochemical and photoelectrochemical measurements and in the dissolution experiments. Pyrite was synthesized by reacting ferric and sulfide ions in aqueous solution at room temperature. The details of pyrite synthesis are described elsewhere (28). Generally, a batch of pyrite samples was made in 50 ml vials. Each contained 10 ml 0.1 M FeCl₃ and 20 ml 0.1 M NaHS solutions at pH 4.0. After aging the solutions for 5 days, pyrite was well formed and precipitated in the bottom of the vials. The pyrite particles were separated from the solution by decanting out the liquid. The particles were then washed several times with O₂-free water and then dried in a vacuum oven at room temperature. Each vial contained 45 mg solid material. The pyrite sample thus prepared was purified further by solvent extraction to remove elemental sulfur (29-32). The extraction was conducted at 47°C in a Soxhlet apparatus with 270 mg solid and 60 ml CS₂. The suspension was agitated with a
magnetic stirrer for 2 hours. Following solid/liquid separation, the purified pyrite particles were washed with carbon disulfide first, then with acetone and oxygen-free water. To prevent oxidation of the sample, all the above processing was conducted in a nitrogen atmosphere. Typically, a 180 mg sample of pyrite was obtained after purification. The pyrite sample contained 99.46% FeS₂ with an average particle diameter of 1.5 μm.

**Electrochemical and Dissolution Measurements**

The electrochemical and dissolution experiments were carried out in an electrochemical cell as illustrated in Fig. 1. The 100 ml Pyrex H-cell consisted of two chambers separated by a fine porosity glass frit, as used by Ward et al.(33). This arrangement confined the pyrite particles to the main chamber. A platinum grid inert electrode with an area of 2 cm² and a saturated calomel reference electrode (SCE) were in the main chamber and a platinum grid counter-electrode was in the other chamber. The current density reported in this work was based on the area of the inert platinum electrode. A flat optical window, located on the wall on the main chamber, allowed light to go directly into the cell. The light source was an Oriel 250 W halogen lamp.

A model 273 Potentiostat /Galvanostat (EG&G Princeton Applied Research), controlled by a computer with a model 352 corrosion analysis software, was used to conduct the electrochemical measurements. In the dissolution measurements, a constant potential was maintained during the experiment and the electrode current was recorded as a function of time. At timed intervals, a liquid sample of 2 ml was taken from the reaction solution with a syringe connected to a 0.2 μm filter. The concentration of the dissolved Fe in solution was determined by atomic absorption spectroscopy (AA).
Non-Aqueous Solution Experiments

Acetonitrile, CH$_3$CN, and tetra-n-butylammonium perchlorate, (C$_4$H$_9$)$_4$NClO$_4$), were used as the non-aqueous solvent and an electrolyte, respectively. Acetonitrile solutions with different water contents were prepared by mixing certain volumes of 1 M aqueous HNO$_3$ solutions with acetonitrile solvent. The final solutions contained 0.1 M (C$_4$H$_9$)$_4$NClO$_4$ electrolyte. Electrochemical measurements carried out in the electrochemical cell were performed using the same procedure described previously.

Characterization of Reaction Products

The reaction products were analyzed and characterized with X-ray diffraction (Rigaku Geigerflex) and a Topcon SX-40A scanning electron microscope (SEM). The samples for X-ray diffraction and SEM were prepared by collecting the solid products from the electrochemical cell after reaction. The solids were then separated from the liquids and dried in a vacuum oven at room temperature.

RESULTS AND DISCUSSION

Electrochemical and Chemical Dissolution

The effect of illumination on the anodic dissolution of pyrite in 1 M HNO$_3$ solution at a potential of 1.0 V(SCE) is shown in Fig. 2. It is observed that the dissolved Fe concentration under illumination is higher than that in the dark. The effect of illumination on the anodic current density under the same conditions is shown in Fig. 3. An increase in
anodic current was also observed under illumination. The pyrite synthesized by the Fe$^{3+}$/HS$^{-}$ reaction is an n-type semiconductor, and the anodic dissolution of pyrite involves the valence band hole reaction (34). Illumination enhances the concentration of the minority carriers (holes) in the valence band of the solid, thus promoting the anodic dissolution rate of pyrite.

The current density shown in Fig. 3 can be converted to the dissolved Fe concentration. Assuming that the overall electrochemical oxidation of FeS$_2$ by holes involves a two-electron transfer process (reactions involving more electrons will be discussed later):

$$\text{FeS}_2 + 2h^+ \rightarrow \text{Fe}^{2+} + 2S^0$$  \[3\]

and the rate of electron transfer from the conduction band of pyrite to the inert electrode is the same as that of the hole reaction with the pyrite lattice, then the total charge, Q in coulombs, from reaction [3] is given by Faraday's law as:

$$Q = z \cdot F \cdot W_{Fe} / M$$  \[4\]

where F is the Faraday constant, M the molecular weight of Fe, $W_{Fe}$ the weight of dissolved Fe in grams and z the number of electrons involved in the reaction. The total charge, Q, for a given time, t in seconds, can be calculated by:

$$Q = S \int i(t) \, dt$$  \[5\]
where \( i(t) \) is the measured current density in A/cm\(^2\) and \( S \) the area of the inert electrode in cm\(^2\). The dissolved Fe concentration, \([Fe]\) in mg/l, in 100 ml solution can be expressed as:

\[
[Fe] = \frac{W_{Fe} \times 10^4}{M \cdot S \cdot 10^4 / (z \cdot F) \int i(t) \, dt}
\]

From Eqs. [4],[5] and [6], we have:

\[
[Fe] = \frac{M \cdot S \cdot 10^4}{(z \cdot F) \int i(t) \, dt}
\]

The current density as a function of time was obtained by curve-fitting the data in Fig. 3. In this particular case, \( M=55.85 \, \text{g mol}^{-1}, S=2 \, \text{cm}^2, z=2, \) and \( F=96500 \, \text{C mol}^{-1} \), the dissolved Fe concentration contributed by electrochemical reaction [3] was calculated according to Eq. [7]. The results, along with the dissolved Fe concentration from direct measurements are shown in Fig. 4. It can be seen that the dissolved Fe concentrations both under illumination and in the dark are lower than the corresponding Fe concentrations that were measured directly. To further confirm this dissolution behavior, an inert electrode potential of 0.8 V(SCE) was applied instead of the 1.0 V(SCE) used in the previous experiments. The current density as a function of time is shown in Fig. 5. A comparison of the calculated and measured Fe concentrations is shown in Fig. 6. The same trend was observed as shown in Fig. 4.

It must be pointed out that the assumed reaction (Eq. [3]) involved the transfer of two electrons. If the overall electrochemical oxidation of pyrite involves more electrons (e.g., Eq. [2]), the dissolved Fe concentration calculated from Eq. [7] will be even smaller. This strongly suggests that the dissolution of pyrite in aqueous solution involves not only an electrochemical process, but also a chemical process. Semiconductor dissolution may
involve both chemical and electrochemical reactions. In a recent study, Allongue and co-workers (35) found that chemical and electrochemical reactions coexist in the oxidation of n-type silicon.

A possible mechanism for pyrite dissolution by a non-electrochemical pathway may involve surface complexation of hydrogen ions. The adsorption of hydrogen ions on the pyrite surface may break the Fe-S bond and subsequently dissolve pyrite according to the following reactions:

\[
\text{FeS}_2 + H^+ \rightarrow \text{FeS}_2: H^+_{(ads)} \quad [8]
\]
\[
\text{FeS}_2: H^+_{(ads)} \rightarrow \text{Fe}^{2+}. \text{HS}^- \rightarrow \text{Fe}^{2+} + \text{HS}_2^-(aq) \quad [9]
\]

The surface hydropolysulfide may decompose to form elemental sulfur (Eq. [10]) or, by further reaction, produce polysulfides (Eq. [11]).

\[
\text{HS}_2^- \rightarrow S^0 + \text{HS}^- \quad [10]
\]
\[
2S^0 + \text{HS}_2^- \rightarrow S_4^{2-} + H^+ \quad [11]
\]

Therefore, it is important to recognize that the elemental sulfur and polysulfides observed by some investigators (21, 26) may come not only from the electrochemical processes (e.g., Eq. [3]), but also from the chemical dissolution processes as shown in Eqs. [8] to [11].

Chemical dissolution via surface protonation of hydrogen ion has been well established in the dissolution studies of metal oxides and silicates (36-43). However, the surface complexation modeling of metal sulfide dissolution system has received little attention so far (44, 45), despite the extensive studies on the non-oxidative dissolution of
metal sulfides, such as sphalerite (ZnS), galena (PbS) and pyrrhotite (Fe_{1-x}S) (46-49). The non-oxidative dissolution of pyrite via surface complexation may be one of the pathways to produce elemental sulfur and polysulfides as described in Eqs. [10] and [11].

From Fig. 4, it is also evident that in the dark, electrochemical reaction yields about 50% of the dissolved Fe in solution. However, the contribution of electrochemical reaction to pyrite dissolution increases substantially under illumination. In this case, illumination creates holes in the valence band of pyrite, favoring electrochemical reaction (Eq. 3). This further confirms that anodic dissolution of pyrite involves hole reactions. Comparison of Figs. 4 and 6 shows that the chemical dissolution predominates at lower electrode potential (Fig. 6). Obviously, the applied potentials control the electrochemical oxidation, but do not affect the chemical dissolution.

**Autocatalysis of Electrochemical Reaction**

Figs. 3 and 5 show that the anodic current density initially increases with reaction time. A maximum current is observed followed by a decrease in current. The increase in current density indicates that an autocatalysis reaction occurs during the anodic dissolution of pyrite. The autocatalytic process is illustrated in Fig. 7, where E_c and E_v refer to the bottom of the conduction band and the top of the valence band of pyrite, respectively. When the potential of the inert electrode (Pt) was maintained at a more positive value than E_c (E_c=0.34 V(SCE) at pH 0 (34), pyrite dissolved to release Fe^{2+} ions in aqueous solution. The ferrous ions would be oxidized to Fe^{3+} at the inert electrode/solution interface. The ferric ions then acted as an oxidant for pyrite by receiving electrons from the conduction band, and were reduced to Fe^{2+}. In other words, the Fe^{2+}/Fe^{3+} couple worked as an electron transfer medium between the inert electrode and the pyrite particles, when the
pyrite particles were not in contact with the electrode. As the reaction proceeded, the concentration of Fe$^{2+}$ increased. As a result, the anodic current increased with the time. On the other hand, the depletion of the pyrite sample would cause a decrease in the current as the dissolution reaction proceeded. This autocatalysis behavior in the pyrite oxidation system was also observed by Lalvani (50).

**Pyrite Dissolution in Acetonitrile Solutions**

The polarization curves of pyrite in acetonitrile solutions with and without illumination are shown in Figs. 8 and 9, respectively. It can be seen that small anodic currents were generated in the absence of water in the solutions. However, when the solutions contained 20% aqueous 1 M HNO$_3$, large anodic currents were observed. The small current generated in the absence of water indicates that reaction [3], which does not involve water, does not proceed at a significant rate. The essential role of water in the process of electrochemical dissolution of pyrite has been stressed by Mishra and Osseo-Asare (16). According to their theory, pyrite dissolution involves several steps. In the first step, pyrite reacts with water via the interaction of iron 3d states with the hydroxyl group of water:

$$\text{FeS}_2 + \text{H}_2\text{O} + \text{h}^+ = \text{Fe(OH)}\text{S}_2 + \text{H}^+$$  \[12\]

In the second step, the OH groups are rearranged on the pyrite surface and move next to the S$_2^{2-}$ sites in the pyrite lattice:

$$\text{Fe(OH)}\text{S}_2 = \text{FeS}_2(\text{OH})$$  \[13\]
Finally, the complete hydroxylation of the surface, followed by oxidation of $S_2^{2-}$ takes place according to the following reactions:

\[
\text{FeS}_2(\text{OH}) + 3\text{H}_2\text{O} + 3h^+ = \text{Fe(OH)}_2\text{S}_2(\text{OH})_2 + 3\text{H}^+ \quad [14]
\]

\[
\text{Fe(OH)}_2\text{S}_2(\text{OH})_2 + 2h^+ = \text{Fe}^{2+} + \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ + \text{H}_2\text{O} \quad [15]
\]

Thiosulfate may either be oxidized further to sulfate through a series of sulfur oxyanions or it may decompose to produce elemental sulfur and bisulfate (16). However, it is also possible that following reaction [13], the polysulfide, $S_2^{2-}$, may be oxidized directly by the hydroxyl radical, OH, to form elemental sulfur:

\[
\text{FeS}_2(\text{OH}) + \text{H}_2\text{O} + h^+ = \text{FeS}_2(\text{OH})_2 + \text{H}^+ \quad [16]
\]

\[
\text{FeS}_2(\text{OH})_2 + 2h^+ = \text{Fe}^{2+} + 2\text{S}^0 + 2\text{H}_2\text{O} \quad [17]
\]

Further insight into the effects of illumination and water on the anodic current densities may be gained by replotting the data of Figs. 8 and 9, as indicated in Figs. 10 and 11. It is obvious that the increase in anodic current density under illumination in the presence of 20% aqueous 1M HNO$_3$ (Fig. 10) is much larger than that in the absence of water (Fig. 11). This indicates that the water and holes are both essential elements for anodic dissolution of pyrite. The experimental data are consistent with Eq. [12]. The anodic current densities are shown as a function of time in Figs. 12 and 13. It can be seen that the anodic current increases dramatically in the aqueous solution. The currents observed in non-aqueous solutions were of negligible magnitude compared with the current in aqueous solution.
Dissolution Products

One of the advantages of using microelectrodes (as opposed to planar electrodes) to study pyrite dissolution is that more products will form from the reaction because of the overall enlarged interface between solid and solution. The solid products from pyrite dissolution can be analyzed by X-ray diffraction technique, and observed directly from SEM photographs.

The X-ray diffractograms of the solid products from the reaction in aqueous solution are shown in Fig. 14 for different acidities. It is observed that elemental sulfur forms at pH 0 (Fig. 14a). However, no elemental sulfur was observed at pH 12 (Fig. 14c). The X-ray diffractograms of the reaction products from acetonitrile solution experiments are shown in Fig. 15. No elemental sulfur was produced in the absence of water in the solutions, while elemental sulfur was observed when the solution contained 20% aqueous 1 M HNO₃. The X-ray diffractograms have clearly shown that elemental sulfur is one of the products from anodic dissolution of pyrite in aqueous solution at low pH. As discussed previously, pyrite dissolution in aqueous solutions at low pH may involve at least two processes; the chemical dissolution via the surface complexation of the proton, and electrochemical oxidation via hole reactions. It is postulated that the hydropolysulfide, HS₂⁻, produced from the pyrite surface protonation by hydrogen, is further decomposed to form elemental sulfur via the chemical reactions as shown in Eqs. [8] to [10]. Formation of elemental sulfur from the electrochemical reaction may be a result of the hole oxidation of lattice S₂²⁻ (Eq. [3]). The holes must be transferred by the hydroxyl radical, OH, from the Fe 3d state to the S₂²⁻ sites. Alternatively, elemental sulfur
could form by the decomposition of thiosulfate as proposed by Mishra and Osseo-Asare (16).

The SEM photographs (Fig. 16) show that the dissolution reaction produces porous surfaces on the pyrite particles (Fig. 16b). When the reaction time is long enough, elemental sulfur becomes the main solid product from the dissolution process (Fig. 17).

CONCLUSIONS

The anodic dissolution of pyrite in acidic solution was studied using microsize particles of pyrite as electrodes. The electrochemical and dissolution experiments showed that pyrite dissolution in acidic solution involved both electrochemical and chemical processes. Under illumination at a high potential, electrochemical oxidation predominates in the overall dissolution process. This is because more holes are created in the valence band of the pyrite by photo excitation. The electrochemical oxidation of pyrite is believed to occur via the hole reaction, unlike chemical dissolution which may take place via the surface complexation of hydrogen ions to break Fe-S bonds.

Pyrite dissolution requires the presence of water. The direct reaction of $S_2^{2-}$ with holes in the pyrite lattice is not significant in the overall oxidation process. The essential role of water in pyrite dissolution can be attributed to the hydroxyl groups (16). Their role, as intermediates, enables the transfer of the holes from pyrite non-bonding orbitals to the $S_2^{2-}$ sites, resulting in oxidation of the sulfides. On the other hand, the lack of hydrogen and/or hydroxyl ions in non-aqueous solution depresses the chemical dissolution process.

Elemental sulfur was directly determined through X-ray diffraction to be a dissolution product of pyrite in acidic solution. Elemental sulfur may be produced both from electrochemical and from chemical reaction.
ACKNOWLEDGMENTS

Support of this work by the United States Department of Energy under Grant No. DE-FG 22-91 PC 91303 is gratefully acknowledged.
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Scan rate: 5 mV/s
180 mg FeS₂
20% 1 M HNO₃

DARK
LIGHT

Fig. 10. Effect of illumination on anodic current density in acetonitrile containing 20% aqueous 1 M HNO₃.
Fig. 11. Effect of illumination on anodic current density in acetonitrile.

Scan rate: 5 mV/s
180 mg FeS$_2$
Without H$_2$O

Acetonitrile / 0.1 M (C$_4$H$_9$)$_4$N${\text{ClO}_4}$

DARK
LIGHT
Fig. 12. Anodic current densities as functions of time under illumination at $E=1.0 \text{ V(SCE)}$. 
Fig. 13. Anodic current densities as functions of time in the dark at $E=1.0\ V(SCE)$. 

- $E = 1.0\ V(SCE)$
- 180 mg FeS$_2$
- Without illumination

- ■ aqueous (1 M HNO$_3$)
- □ non-aqueous
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