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R. H. Yoon and P. E. Richardson
Department of Mining and Minerals Engineering
Virginia Polytechnic Institute & State University
Blacksburg, Virginia 24061-0258

by

TECHNICAL PROGRESS REPORT

for the Ninth Quarter
(October 1, 1994 to December 31, 1994)
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ABSTRACT

The major objectives of this work are i) to determine the Eh-pH conditions under which pyrite is stable, ii) to determine the mechanism of the initial stages of pyrite oxidation, and iii) to determine if the semi-conducting properties of pyrite effects its oxidation behavior. It is known that moderate oxidation of pyrite produces a hydrophobic surface product. This hydrophobic product makes it extremely difficult to depress pyrite in coal flotation circuits. The eventual objective of this work is to prevent pyrite oxidation in order to better depress pyrite in coal flotation circuits.

In this work clean, unoxidized pyrite surfaces are being produced by fracturing pyrite electrodes in an electrochemical cell. It has been shown that pyrite assumes a unique potential, referred to as the “stable potential” at the instance it is fractured and that this potential is several hundred millivolts more negative than the steady state mixed potential of pyrite. It has also been shown that by holding the potential of pyrite at its stable potential during fracture, pyrite undergoes neither oxidation nor reduction. It has also been found that fresh pyrite surfaces created by fracture in an electrochemical begin to oxidize at potentials that are about 200 mV more negative than the potentials reported in the literature for pyrite oxidation. This is attributed to the fact that most work on pyrite has employed polished electrodes that have pre-existing oxidation products on the surface. Electrochemical reduction and oxidation of these pre-existing products essentially mask the oxidation of pyrite itself. In addition, photocurrent measurements show that freshly fractured pyrite surfaces are charged negatively. This negative charge is believed to result from an intrinsic, acceptor-like surface state.
This report period, electrochemical impedance spectroscopy (EIS) studies were continued. As discussed in the seventh quarterly progress report, the impedance of pyrite does not show the characteristics expected for either semi-conducting or metallic electrodes. Additional studies were conducted to confirm the anomalous impedance behavior. For this purpose, freshly fractured surfaces were progressively polished on 600 and 1200 grit silicon carbide paper, and with 0.3 \( \mu \) \( \alpha \)-alumina and 0.05 \( \mu \gamma \)-alumina micropolish. Polishing is known to introduce defects in the lattice structure of semi-conducting electrodes and it was anticipated that the defects would effect the interfacial capacitance.
TABLE OF CONTENTS

ABSTRACT ................................................................................................................... i

TABLE OF CONTENTS ................................................................................................. iii

LIST OF FIGURES ......................................................................................................... iv

LIST OF TABLES ............................................................................................................ v

Introduction .................................................................................................................. 1

Objective of this Report Period ................................................................................... 2

Experimental ................................................................................................................ 2

Results and Discussion .............................................................................................. 2

Effect of the pH on the EIS spectra of pyrite ............................................................... 10

Conclusion ................................................................................................................... 12

Future Work ................................................................................................................ 12
LIST OF FIGURES

Figure 1. Complex plane impedance plots of pyrite for freshly fractured and polished electrode at 0 V (SHE). Pyrite from Spain with surface prepared by \textit{in-situ} fracture near stable potential 0 V) in pH 4.6 butter solution and progressive polishing with 600 and 1200 grit silicon carbide paper, and 0.3 \( \mu \) \( \alpha \)-alumina and 0.05 \( \gamma \)-alumina micropolish. ................................................................. 6

Figure 2. Complex plane impedance plots of pyrite for freshly fractured and polished electrode at -0.60 V (SHE). Same electrode as used in Figure 1. .................... 6

Figure 3. Complex plane impedance plots of pyrite for freshly fractured and polished electrode at 0.85 V (SHE). Same electrode as used in Figures 1 and 2. .......... 7

Figure 4. The schematic diagrams of equivalent electrical circuits for:
(a) simple electrochemical system,
(b) simple electrochemical system with a product layer on electrode surface,
(c) simple electrochemical system with induced lattice defects in the space charge region of the electrode surface. ........................................... 9

Figure 5. Complex plane impedance plots of a freshly fractured pyrite electrode as it is progressively reduced at potentials -0.28 V to -0.80 V (SHE). Pyrite from Spain with surface prepared by \textit{in-situ} fracture near stable potential (-0.28 V) in pH 9.2 buffer solution. ................................................................. 10

Figure 6. Complex plane impedance plots of a freshly fractured pyrite electrode as it is progressively oxidized at potentials -0.28 V to 0.40 V (SHE). Same electrode as used in Figure 5. ......................................................... 11

Figure 7. Complex impedance plots of a freshly fractured pyrite electrode as it is aggressively reduced at -1 V and aggressively oxidized at 0.75 V. Same electrode as used in Figure 5 and 6. ......................................................... 11
LIST OF TABLES

Table 1. The impedance values calculated for the equivalent circuit from the impedance plots in figure 1-3 using Boukamp's 'Equivalent Circuit' software.

7
Introduction

One of the major problems hindering the development of an advanced flotation process for separating pyrite from coal is the "self-induced" or collectorless flotation of pyrite. It is known that collectorless flotation results from the moderate oxidation of pyrite, but the oxidation products and conditions required to prevent pyrite oxidation and subsequent collectorless flotation are not known. One of the reasons why the reactions are not better understood is that most pyrite that has been studied has been previously oxidized. For example, electrochemical studies are usually employed to study pyrite oxidation and most of these studies have been made on polished electrodes. The polishing process is known to produce ferric oxide, Fe₂O₃, and ferric hydroxide, Fe(OH)₃, on pyrite. These are hydrophilic compounds. It is not known what happens to the pyritic sulfur during polishing, but it is believed that an oxidation product of sulfur is responsible for collectorless flotation.

In flotation circuits, fresh surfaces are produced by grinding immediately before flotation, which is believed to produce surfaces that are much different than those produced by abrasion or polishing.

The present studies avoid pre-existing oxidation products on pyrite by using an in-situ fracture technique that produces virgin pyrite surfaces in the electrochemical cell. The electrodes are potentiostated at pre-selected values prior to and during fracture. It has been found that there is a specific potential at which a freshly-produced pyrite surface neither undergoes reduction nor oxidation. Essentially, no current is passed on electrodes potentiostated at this specific potential during fracture. Electrodes held at more positive potentials than this value undergo spontaneous
oxidation, while electrodes held at more negative potentials undergo spontaneous reduction. It was also shown by photocurrent measurements that a negative surface charge exists on pyrite surfaces that are produced by *in-situ* fracture at pH 4.6 and 9.2 and that one method to reduce this negative charge was to cathodically decompose pyrite.

**Objective of this Report Period**

As discussed in the seventh quarterly progress report, the impedance of pyrite shows characteristics of neither semi-conducting nor metallic electrodes. The objective of the research during this report period was to further study the anomalous impedance behavior of pyrite.

**Experimental**

Pyrite samples from Spain were obtained from Geoscience Resources and rectangular electrodes of each of the pyrites prepared using a slow-speed diamond saw. Samples of each of the pyrites were mounted as electrodes for *in-situ* fracture. The electrodes were fractured in a nitrogen sparged pH 4.6 acetic acid-acetate buffer solution. Freshly fractured electrodes were progressively polished on 600 and 1200 grit silicon carbide paper, and 0.3 μ α-alumina and 0.05 γ-alumina μ micropolish. Additionally, freshly fractured pyrite was studied in pH 9.2 sodium tetraborate solution.

**Results and Discussion**

As discussed in the seventh quarterly report, impedance studies were conducted on *in-situ* fractured photosensitive pyrite from Mexico in pH 4.6 buffer solution. The electrode was then polished on 600 grit silicon carbide and its impedance determined over the range of 0 V to slightly oxidizing potentials of 0.05, 0.15, 0.25 V. It was observed that the freshly fractured
electrode surface was very sensitive to very moderate oxidation of pyrite and that oxidation caused a slight decrease in the slope of complex impedance plots. In contrast, moderate oxidation (from 0 to 0.25 V) of the polished electrode had almost no effect on the complex impedance. Insensitivity to oxidation potentials probably indicates that the surface already has an oxidation layer due to polishing. As explained in seventh progress report polishing causes an increase in the area of the electrode surface, which causes a corresponding decrease in both, the real and the imaginary components of the impedance. This is consistent with the simple geometric capacitance of parallel plates,

\[ C_{dl} = \frac{\varepsilon A}{d} \]  

where \( \varepsilon \) is the dielectric constant, A the area and d the distance between the plates.

The capacitive reactance is given by:

\[ X_C = -j \frac{wC_{dl}}{d} \]  

Similarly, the ohmic reactance is given by:

\[ X_R = R = \frac{\rho d}{A} \]  

where \( \rho \) is the resistivity.

Thus an increase in area will result in decrease in both the capacitive (imaginary component) and the ohmic (real component) impedances.

However, the impedance plots for freshly fractured and polished surfaces cannot be scaled to completely overlap each other by multiplication with an area factor. This suggests that real changes in reactivity or chemical structure of the pyrite surface occurs. Lattice defects may
also be induced in the space charge region by polishing. This is consistent with the photoelectric studies, which show a large reduction in photocurrent with polishing.

To better understand the impedance of pyrite, another electrode was fractured \textit{in-situ} and its impedances determined at -0.60 V, 0 V and 0.85 V. The electrode was then wet polished progressively with 600 grit and 1200 grit silicon carbide paper, and 0.3 $\mu$ $\alpha$-alumina and 0.05 $\mu$ $\gamma$-alumina micropolish. After each polishing, the impedance was measured at -0.60, 0 and 0.80 V. Figure 1-3 show the impedance plots for freshly fractured and polished electrode at 0, -0.60 and 0.85 V, respectively.

As it can be seen from figure 1, the impedance plots at 0 V are nearly linear consistent with previous results. For pyrite, it is believed that the linear behavior is due to a very large charge transfer resistance due to the irreversible behavior of the surface reactions. As reported in the seventh quarter, at pH 4.6 pyrite is nearly inert over a wide range of potential (-0.45 to 0.65 V), in contrast to its voltammogram that indicates that surface reactions occur in this range of potentials. The inert response of pyrite to the sinusoidal signal used to measure the impedance can be explained as follows. In EIS, an AC signal of 5 to 20 mV (peak to peak) is applied to the electrode held at selected potentials. The surface product is oxidized by the first positive cycle of the AC signal. However, because the surface oxidation reactions are so irreversible, the product is not reduced on the negative cycle. Moreover, no further oxidation or reduction takes place on subsequent cycles of the AC signal. Thus, due to the irreversible behavior of the surface product, the electrode surface exhibits a nearly inert nature and a very large charge transfer resistance.
At -0.60 V, well defined semicircular impedance plots are obtained (figure 2). The diameter of the semicircular impedance plot, i.e., the charge transfer resistance, increases with finer polishing of electrode and approaches that of the freshly fractured electrode after polishing with 0.3 μ micropolish. Figure 3 shows the impedance plots at 0.85 V, which follow a similar trend. Interestingly, the impedance plot for 0.05 μ polishing does not behave in the manner described above. Also, the impedance plot for fine polishing (0.3 μ micropolish) does not overlap with that of freshly fractured electrode. This indicates that the polishing induces changes other than simply affecting the surface area of the electrode.

An equivalent electrical circuit for the simplest electrochemical system consists of three components, i.e., $R_s$, the series resistance due to solution and electrical connections, $R_p$, the polarization resistance of the surface in parallel with $C_{dl}$, the double layer capacitance (Figure 4 (a)). The polarization resistance, $R_p$, is inversely related to the surface reaction rate. The double layer capacitance, $C_{dl}$, consists of the space charge layer capacitance, Helmholtz layer capacitance and Gouy layer capacitance. Table 1 shows the impedance values calculated for the equivalent circuit from the impedance plots in figure 1-3. The calculations were made using Boukamp’s ‘Equivalent Circuit’ software. Interestingly, the calculated capacitance values depend on the frequency. The frequency dependent interfacial capacitance is usually interpreted
Figure 1. Complex plane impedance plots of pyrite for freshly fractured and polished electrode at 0 V (SHE) in pH 4.6 buffer solution.

Figure 2. Complex plane impedance plots of pyrite for freshly fractured and polished electrode at -0.60 V (SHE).
Figure 3. Complex plane impedance plots of pyrite for freshly fractured and polished electrode at 0.85 V (SHE).

Table 1.: The impedance values calculated for the equivalent circuit from the impedance plots in figure 1-3 using Boukamp’s ‘Equivalent Circuit’ software.

<table>
<thead>
<tr>
<th></th>
<th>Impedance</th>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>0 V</td>
<td>-0.60 V</td>
<td>0.85 V</td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td></td>
<td>$R_p$</td>
<td>$Y_0$</td>
<td>$n$</td>
<td>$R_p$</td>
<td>$Y_0$</td>
<td>$n$</td>
<td>$R_p$</td>
<td>$Y_0$</td>
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</tr>
<tr>
<td>Freshly fractured</td>
<td>$1.3 \times 10^{20}$</td>
<td>17.5</td>
<td>0.76</td>
<td>$4.65 \times 10^{20}$</td>
<td>27.5</td>
<td>0.73</td>
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<td>600 grit S-C paper</td>
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<td>37.1</td>
<td>0.84</td>
<td>$2.95 \times 10^{25}$</td>
<td>35.1</td>
<td>0.78</td>
<td>$4.87 \times 10^{25}$</td>
<td>21.2</td>
<td>0.85</td>
</tr>
<tr>
<td>1200 grit S-C paper</td>
<td>$1.5 \times 10^{27}$</td>
<td>30.8</td>
<td>0.75</td>
<td>$4.53 \times 10^{27}$</td>
<td>34.2</td>
<td>0.78</td>
<td>$5.56 \times 10^{27}$</td>
<td>25.4</td>
<td>0.79</td>
</tr>
<tr>
<td>0.3 μ micropolish</td>
<td>$1.4 \times 10^{8}$</td>
<td>19.0</td>
<td>0.75</td>
<td>$4.07 \times 10^{8}$</td>
<td>28.0</td>
<td>0.84</td>
<td>$5.31 \times 10^{8}$</td>
<td>19.0</td>
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<tr>
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<td>$116$</td>
<td>27.8</td>
<td>0.71</td>
<td>$68.92$</td>
<td>42.0</td>
<td>0.77</td>
<td>$111$</td>
<td>63.7</td>
<td>0.70</td>
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<tr>
<td>0.05 μ micropolish</td>
<td>$4 \times 10^{4}$</td>
<td>20.7</td>
<td>0.86</td>
<td>$4.26 \times 10^{4}$</td>
<td>22.8</td>
<td>0.91</td>
<td>$3.06 \times 10^{4}$</td>
<td>30.8</td>
<td>0.85</td>
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<tr>
<td></td>
<td>$91.4$</td>
<td>28.9</td>
<td>0.72</td>
<td>$91.9$</td>
<td>132.4</td>
<td>0.63</td>
<td>$60$</td>
<td>63.6</td>
<td>0.74</td>
</tr>
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</table>

The series resistance, $R_s$, is 50 - 60 Ω. The units for $R_p$ is ohms and that of $Y_0$ is (megaohms)$^{-1}$.  

Center for Coal and Minerals Processing  

July 1995
in terms of the roughness of the surfaces. The reactance of the frequency dependent capacitance is given by:

\[
Z_c = \frac{1}{Y_0(jw)^n}
\]  

where,

\[
Y_0 = \text{the admittance, independent of frequency},
\]

\[
w = \text{the angular frequency},
\]

\[
n = \text{a fitting constant used to separate the real and imaginary component of } Z_c,
\]

\[
j = \text{square root of } -1, \text{ a complex number}.
\]

Further analysis of the impedance plots after polishing with 0.3 and 0.05 μ micropolish indicates that the simple equivalent electrical circuit, as shown in figure 4 (a), is not sufficient to explain the interface. Table 1 suggests that there exists another RC circuit in series with the simple electrical circuit. This indicates that fine polishing induces (i) a product layer on the surface which can be represented by \( R_XC_X \) (Figure 4 (b)), or (ii) the defects in the space charge region, characterized by \( R_{SC}C_{SC} \) (Figure 4 (c)). These defects can act as traps for charge carriers and will cause a decrease in the impedance (increase in capacitance), as observed by impedance plots after polishing with 0.05 μ micropolish.
Figure 4. The schematic diagrams of equivalent electrical circuits for:
(a) simple electrochemical system,
(b) simple electrochemical system with a product layer on electrode surface,
(c) simple electrochemical system with induced lattice defects in the space charge region of the electrode surface.
Effect of the pH on the EIS spectra:

Impedance experiments for freshly fractured pyrite electrodes were conducted in pH 9.2 buffer solution. The ‘stable potential’ at pH 9.2 is near -0.28 V. Pyrite was fractured near the stable potential and was progressively reduced at potential between -0.28 V and -1.0 V and progressively oxidized between -0.28 V and 0.75 V. Figures 5, 6 and 7 show the impedance plots for moderate reduction (-0.28 V to -0.80 V), moderate oxidation (-0.28 V to 0.60 V) and aggressive reduction and oxidation (-1 V and 0.75 V), respectively. As it can be seen impedance plots are nearly linear over a wide range (-0.80 V to 0.40 V), establishing again that pyrite is nearly inert to the AC signal in this potential range. It is not until the potential reaches -1.0 V on reduction side and 0.5 V on oxidation side that the impedance plots assume a definite semicircular

![Complex plane impedance plots](image)

Figure 5. Complex plane impedance plots of a freshly fractured pyrite electrode as it is progressively reduced at potentials -0.28 V to -0.80 V (SHE) in pH 9.2 buffer solution.
Figure 6. Complex plane impedance plots of a freshly fractured pyrite electrode as it is progressively oxidized at potentials -0.28 V to 0.40 V (SHE) in pH 9.2 buffer solution.

Figure 7. Complex plane impedance plots of a freshly fractured pyrite electrode as it is aggressively reduced at -1 V and aggressively oxidized at 0.75 V in pH 9.2 buffer solution.
semicircular shape. These results are consistent with the behavior of pyrite in pH 4.6 buffer solution except that the potential range is wider and is shifted towards more negative values. This is due to the fact that the surface electrochemical reactions occur at more negative potentials at higher pH.

Conclusion

Electrochemical impedance spectroscopy of pyrite shows that the polishing of the electrode surface effects its impedance spectra. The effects of polishing are believed to be:

(i) change in the surface area of the electrode, which changes both the real and the imaginary impedances,

(ii) formation of an oxidized product layer on the electrode surface, which introduces another RC circuit in series with the simple equivalent electrical circuit,

(iii) induced lattice defects in space charge region, which increases the space charge layer capacitance and introduces another RC circuit in series with simple equivalent electrical circuit.

It is also shown that in pH 9.2 solution pyrite is inert to the AC signal over a wide range of potentials and that its charge transfer resistance decreases significantly when it is aggressively oxidized or reduced. This result is consistent with the previously reported impedance results.

Future Work

Research to interpret the impedance spectroscopy of pyrite electrodes is continuing. Research has been initiated to study the effect of corrosion inhibitors on the initial potential pyrite assumes at fracture and on its subsequent oxidation characteristics.
CAPTION OF FIGURES

Figure 1. Complex plane impedance plots of pyrite for freshly fractured and polished electrode at 0 V (SHE) in pH 4.6 buffer solution.

Figure 2. Complex plane impedance plots of pyrite for freshly fractured and polished electrode at -0.60 V (SHE)

Figure 3. Complex plane impedance plots of pyrite for freshly fractured and polished electrode at 0.85 V (SHE).

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