ELECTROCHEMICAL AND RAMAN INVESTIGATION OF PYRITE AND CHALCOPYRITE OXIDATION

by

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Abstract

The electrochemical behavior of chalcopyrite and pyrite in acidic ferric solutions was investigated using leaching experiments, electrochemical techniques and micro Raman spectroscopy.

The investigation of pyrite-assisted leaching of chalcopyrite concentrate in iron sulfate showed that the catalytic effect of pyrite varies depending on the source of the sample. Cyclic voltammetry using solid paraffin carbon paste electrode demonstrated that the ability of chalcopyrite to reduce ferric ions declines with time spent in the leaching reactor.

Single particle microelectrode technique was employed to investigate the electrochemical and semiconducting properties of different pyrite samples by means of cyclic voltammetry, electrochemical impedance spectroscopy and Mott-Schottky methods. Cyclic voltammetry showed a difference in the magnitude of the ferric reduction reaction peaks. An equivalent analogue circuit was used to model the impedance spectra, which led to the conclusion that pyrite samples with lower charge transfer resistance are better catalysts for ferric reduction.

Micro Raman investigation revealed that elemental sulfur and intermediate products of pyrite oxidation form on the surface of the effective pyrite sample, while sulfur alone forms on the surface of less effective pyrite.

Gold and silver nanoparticles were deposited on pyrite at ambient temperature from colloidal solutions. The modified pyrite was investigated using Electrochemical Impedance Spectroscopy. The results revealed a decrease in charge transfer resistance for the redox couple associated with the modified pyrite.

It is concluded that the inconsistencies observed in the kinetics of chalcopyrite leaching in pyrite-assisted leaching are due to erratic electrocatalytic behavior of pyrite samples from different geographical locations with various chemical compositions. The concordance between observations of sluggish charge transfer between energy levels
in pyrite and electrolyte in less effective pyrite samples in the leaching experiments strengthens the hypothesis that charge transfer between pyrite and the redox couple in solution is the key step in the process.
Preface

In all the publications listed below, the primary investigator and author of the manuscripts was Maziar Eghbalnia, who was responsible for conducting the research, preparing and analyzing the results, and writing the manuscripts. Dr. David G. Dixon provided guidance and editorial input.

Some of the work presented in Chapters 1 to 5 of this thesis has resulted in publication in journal papers or conferences. The following is a list of these publications:

- Eghbalnia, M. and Dixon, D.G., In Situ Electrochemical Characterization of Natural Pyrite as a Galvanic Catalyst Using Single Particle Microelectrode Technique in Ferric Sulfate Solution. Submitted for publication (chapters 3 and 5).
- Eghbalnia, M. and Dixon, D.G., Raman investigation of pyrite oxidation during ferric sulfate leaching of chalcopyrite. Submitted for publication (chapters 3, 4 and 6).
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CHAPTER 1: Introduction

1.1 Problem Definition

Copper is one of the most commonly used metals and demand has continually grown over the last decade. Based on International Copper Study Group (ICSG) data, world copper mine production increased by 18% over a 10-year period, from 13.6 million metric tons (mmt) in 2001 to 16.1 mmt in 2010 (ICSG, 2011). World annual refined copper usage increased by 29% over this decade from 15 mmt to 19.3 mmt with an annual growth rate of 2.9% (ICSG, 2011). Copper possesses many desirable properties, such as the second highest electrical conductivity (59.6 \times 10^6 \text{ S/m}) and thermal conductivity (397 \text{ Wm}^{-1}\text{k}^{-1}) of all the elements, exceptional ductility, strength, and resistance to corrosion and creeping which have increased its usage for a variety of applications, especially in the sectors of electronics, equipment manufacturing, building construction, and infrastructure (Abbaschian \textit{et al.}, 2009). Therefore, it is important to find new methods for copper production and treatment options for low grade or refractory ores to keep up with growing demand for copper, coupled with the depletion of high grade ores.

About 80% of primary copper production comes from pyrometallurgical processing of copper ores. Compared to pyrometallurgy, hydrometallurgy is a relatively new discipline, with the majority of developments taking place in the last century (Schlesinger, 2011).

Hydrometallurgical processes for metal extraction from ores or secondary materials (\textit{i.e.}, concentrates), generally consists of three main steps:

- dissolution of a compound and/or metal value from an ore or concentrate into a leach solution,
- purification and/or upgrading of the leach solution, and
- recovery of value from the purified solution.
Hydrometallurgical processing of copper has been commonly used for oxide minerals such as azurite \((2\text{CuCO}_3\cdot\text{Cu(OH)}_2)\), malachite \((\text{Cu}_2\text{CO}_3\cdot\text{OH})_2\), chrysocolla \((\text{CuO}\cdot\text{SiO}_2\cdot2\text{H}_2\text{O})\), atacamite \((\text{Cu}_2\text{Cl}2\cdot\text{OH})_3\), and sulfide minerals such as chalcocite \((\text{Cu}_2\text{S})\) and covellite \((\text{CuS})\) (Schlesinger, 2011).

Conversely, smelting, converting and electrorefining have been the dominant methods for the extraction of copper from chalcopyrite \((\text{CuFeS}_2)\), the most abundant copper-bearing mineral in the world, since the 19th century (Schlesinger, 2011).

Some of the disadvantages of copper pyrometallurgy include: production of large amounts of gases, unsuitable thermal balance of endothermic and exothermic processes and copper losses into the slag. In spite of the fact that some of the previous disadvantages have been resolved or minimized in modern smelters and pyrometallurgy offers a proven process for chalcopyrite concentrates, there is still significant incentive to formulate an affordable hydrometallurgical process to treat chalcopyrite concentrates. Firstly, a high capital investment is needed for construction of a smelter compared to a hydrometallurgical plant. Secondly, smelters need to be designed to treat large quantities of materials as opposed to hydrometallurgical plants that can be built at the desired scale to minimize capital expense. Thirdly, there are difficulties associated with the emission of gases, and the storage and transport of sulfuric acid produced at smelters. Lastly, the presence of impurities such as arsenic and antimony in concentrates is a growing concern as these render chalcopyrite concentrates less attractive for smelting due to emission and waste standards, and thus incur high penalty fees. As clean deposits are depleted the need to process ore bodies with high impurity levels increases. Therefore, arsenic will be present more frequently in copper concentrates, and finding an environmentally and economically viable process for treating these materials will have a huge impact on the future of the copper industry.

Historically, chalcopyrite has been a difficult mineral to process by hydrometallurgical means. In recent years, extensive research on hydrometallurgical alternatives to the conventional pyrometallurgical processes has been conducted (Dreisinger, 2006). These processes can be categorized based on the type of leaching media used; sulfate,
chloride, nitrate, and ammonia are the most common examples. Sulfate is the most appealing of these, due to the simplicity of the leach chemistry, low capital investment and higher recovery of copper by solvent extraction and electrowinning (Hackl et al., 1995). The main problem associated with chalcopyrite leaching in sulfate media is the slow and incomplete copper extraction. This challenge is caused by the formation of passive layers on the chalcopyrite surface, and the potential blocking and wetting of chalcopyrite by liquid elemental sulfur (Dreisinger, 2006).

Many studies have been conducted to understand the kinetics of chalcopyrite leaching in ferric sulfate media; however, the leaching mechanism, among other fundamental aspects, remains poorly understood. It has been shown previously that chalcopyrite dissolution is electrochemical in nature (Ammou-Chokroum et al., 1977a, 1977b, and 1981; Jones, 1974; Parker et al., 1981a and 1981b). Therefore, it is not unexpected that of all the methods that have been employed to investigate the leaching of chalcopyrite, electrochemical techniques have been the most useful. On the other hand, these studies have also been a source of substantial debate surrounding the nature of the chalcopyrite dissolution mechanism.

1.1.1 Pyrite-assisted Leaching of Chalcopyrite

Dutrizac and MacDonald (1973) investigated the effect of other sulfide minerals such as bornite (Cu$_5$FeS$_4$), cubanite (CuFe$_2$S$_3$), galena (PbS), pyrite (FeS$_2$) molybdenite (MoS$_2$), stibnite (Sb$_2$S$_3$) and sphalerite (ZnS) on the dissolution behavior of chalcopyrite. They prepared sintered pellets with known amounts of various sulfide impurities. They concluded that adding cubanite to chalcopyrite was practically ineffective since chalcopyrite-cubanite mixtures behave almost additively; addition of bornite had a slight beneficial effect. Pyrite, molybdenite or stibnite sped up the chalcopyrite dissolution rate, while the presence of galena impeded its dissolution. High-iron sphalerite somewhat retarded the chalcopyrite dissolution, but the effect of low-iron sphalerites was erratic. They concluded that all of these observations are consistent with a galvanic dissolution mechanism. The only exception was molybdenite which
accelerated the chalcopyrite dissolution but did not follow the galvanic mechanism during dissolution.

Mehta and Murr (1983) carried out potentiodynamic polarization measurements under an acid-bacterial leaching system in order to study the magnitude of galvanic interaction when chalcopyrite (CuFeS$_2$) and pyrite (FeS$_2$) are in contact. They concluded that a mass ratio of 1:1 and a particle size of smaller than 200 mesh were the most optimal conditions when leaching was carried out in the presence of *T. ferrooxidans*. Under these conditions, the dissolution of copper from chalcopyrite was increased by a factor of 2 to 15, thus agreeing with the findings of Dutrizac and MacDonald (1973). However, it did not corroborate their idea that the galvanic interaction between sulfides was the cause of this dissolution enhancement. Mehta and Murr (1983) suggested that the reason for this phenomenon may be that the minerals associated with chalcopyrite in the concentrates changed the dissolution rate by altering the diffusivity or concentration, or both, of the rate controlling species within the chalcopyrite lattice.

Mishra (1973) also examined the effect of mixing pyrite with chalcopyrite. He prepared a mixture consisting of equal proportions of chalcopyrite and pyrite having a total weight of 150 g. The leaching experiments were performed at 80°C in sulfuric acid solutions, and three stages were reported: stage one, a very rapid dissolution, in which it was believed that the galvanic interaction between chalcopyrite and pyrite was occurring; stage two, formation of a layered product insulating the particles was reported, thus inhibiting the galvanic effect and impediment of the dissolution rate; and stage three, in which pyrite was assumed to leach, producing sulfuric acid that dissolved iron salts deposited on the chalcopyrite surfaces, thus accelerating the rate. The total copper dissolved in the presence of pyrite was twice as much as in its absence.

Abraitis et al. (2004a) studied mechanisms of dissolution of pyrite, chalcopyrite, galena and sphalerite in acidic chloride media, focusing on the galvanic effects between pyrite and the other minerals. The dissolution rates for chalcopyrite, galena and sphalerite in the presence of pyrite increased by 18, 31 and 1.5 times, respectively relative to the experiments conducted in the absence of pyrite. They concluded that their results were
in agreement with galvanically-promoted mineral oxidation of the other sulfides in the presence of pyrite.

Some recent studies on usage of pyrite in hydrometallurgy have led to a novel pyrite-assisted atmospheric leaching of primary copper concentrates, known as the Galvanox™ process (Dixon et al., 2008). In this process, atmospheric leaching of copper from chalcopyrite (CuFeS₂) concentrates occurs in an acidic ferric/ferrous sulfate solution. The key to success for this process is the presence of ground pyrite in the leaching reactor. Pyrite is necessary in order to overcome the fundamental problem of chalcopyrite passivation in oxidative leaching processes. Ferric ion is also used as a surrogate oxidant (e.g., a redox catalyst) on behalf of dissolved oxygen. In this process, the addition of pyrite to the leach slurry has a striking effect on copper extraction. The use of atmospheric leaching conditions eliminates the high cost of autoclaves, required for high-temperature, high pressure processes. The low operating temperature and mild chemical conditions allow the near-quantitative yield of elemental sulfur, thus reducing the consumption of oxygen and neutralizing agents. In this process, rapid copper dissolution rates can be achieved compared to other sulfate-based leaching processes. Pyrite plays a critical role in the galvanically-assisted leaching process. Unassisted leaching of chalcopyrite is shown in Figure 1.1 a.

The overall leaching reaction of chalcopyrite dissolution in this process is as follows:

\[ \text{CuFeS}_2 + 4\text{Fe}^{3+} = \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S} \]  
(R1.1)

This reaction may be represented as a combination of anodic and cathodic half-cell reactions.

Anodic half-cell reaction:

\[ \text{CuFeS}_2 = \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S} + 4\text{e}^- \]  
(R1.2)

Cathodic half-cell reaction:

\[ \text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+} \]  
(R1.3)
It is believed that the presence of an alternative, catalytic surface for ferric reduction in electrical contact with chalcopyrite alleviates the passive behavior of chalcopyrite in a ferric sulfate solution. This has been ascribed to the specific properties of pyrite and its role in facilitating the cathodic half-cell reaction (i.e., ferric reduction). Based on the claims of Tshilombo (2004), reaction (R1.3) is the rate determining step, therefore controlling the kinetics of the overall reaction. Pyrite is an effective and convenient source of this alternative surface for ferric reduction. In Figure 1.1 b the assisted leaching process is shown schematically (Dixon et al., 2008).

![Figure 1.1 Schematic diagram of electrochemical leaching of chalcopyrite.](image)

a) in the absence of pyrite

b) in presence of pyrite (with permission from Rivera-Vásquez, 2010).
It is still unknown whether the assisting effect of pyrite on chalcopyrite leaching is due to the galvanic interaction of these two minerals alone. It is generally known that galvanic interactions between minerals (i.e., the formation of galvanic cells) can substantially increase the dissolution rate. In a galvanic cell, the mineral with the lower open circuit potential acts as an anode and dissolves preferentially to the mineral with the higher open circuit potential, which will be protected galvanically. The minerals need to be in electrical contact and immersed in a suitable leaching medium to provide a means for ion migration.

Recent studies conducted by the author on the Galvanox™ process have shown some inconsistencies in the leaching results. It was concluded that pyrite samples from different sources can influence the rate of chalcopyrite leaching differently. Some pyrite samples accelerate the leaching rate significantly, while others have less effect on the process. The research to date has tended to focus on the kinetics of anodic dissolution of chalcopyrite in leaching processes, while little attention has been paid to the kinetics of ferric reduction on the surface of pyrite.

1.2 Objectives of This Investigation

The main objective of this work is to study the electrochemistry of pyrite-assisted leaching of chalcopyrite, the role of pyrite and its semiconductive electrochemistry in ferric sulfate media, and the reasons behind its inconsistent catalytic behavior. Several techniques were developed and evaluated to prepare electrodes from ground sulfide mineral particles to investigate the electrochemical properties of chalcopyrite and pyrite. This main objective was subdivided into the following:

- Determine the catalytic effect of different pyrite samples on the chalcopyrite leaching kinetics
- Undertake detailed comparative studies of the electrochemical response of chalcopyrite electrodes before and during leaching in the absence and presence of pyrite
- Evaluate the electrocatalytic activity of chalcopyrite and pyrite for ferric reduction
- Investigate the surface behavior of various pyrite samples during pyrite-assisted chalcopyrite leaching by micro Raman spectroscopy
- Modify the electrocatalytic properties of pyrite electrodes using gold and silver nanoparticles
CHAPTER 2: Literature Review

2.1 Crystal Structure of Pyrite and Chalcopyrite

Iron atoms in pyrite form crystals with face centered cubic symmetry. The crystal lattice of pyrite resembles the NaCl structure; dumbbell-shaped disulfide ions ($S_2^{2-}$) occupy the chloride positions and the iron atoms occupy the sodium positions. Disulfide ions lie at the center of the cubes and at the mid-points of the cube edges. Each sulfur atom is coordinated with three iron atoms and one other sulfur atom. Each iron atom is coordinated with six sulfur atoms in a tilted octahedron (Vaughan & Craig, 1978). The structure of pyrite is depicted in Figure 2.1. Lowson (1982) reported the interatomic distances given in Table 2.1.

Figure 2.1  Crystal structure of pyrite (adapted from Rickard and Luther, 2007).
Table 2.1 Interatomic distances of pyrite (adapted from Lowson, 1982).

<table>
<thead>
<tr>
<th>Description</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>spacing of the unit cell $a_0$</td>
<td>0.54175 nm</td>
</tr>
<tr>
<td>between two iron atoms on the 110 face</td>
<td>0.382 nm</td>
</tr>
<tr>
<td>between two sulfur atoms of the sulfur pair on the 111 axis</td>
<td>0.206 nm</td>
</tr>
<tr>
<td>between iron and the center of a sulfur pair on the 001 face</td>
<td>0.270 nm</td>
</tr>
<tr>
<td>between adjacent sulfur atoms</td>
<td>0.226 nm</td>
</tr>
<tr>
<td>S-Fe-S bond angle</td>
<td>85.66 to 94.34°</td>
</tr>
<tr>
<td>Fe-S-Fe bond angle</td>
<td>115.5°</td>
</tr>
<tr>
<td>S-S-Fe bond angle</td>
<td>102.4°</td>
</tr>
</tbody>
</table>

The tetragonal body-centered structure of the chalcopyrite bulk structure is derived from the zinc blende structure, with the zinc atoms replaced by iron and copper atoms (Hall and Stewart, 1973). As shown in Figure 2.2, the copper and iron atoms are each bonded to four sulfur atoms and the cubic symmetry of the zinc blende structure is replaced by tetragonal symmetry. The symmetry change takes place because the differing metal radii cause the sulfur atoms to move closer to the iron atoms and further from the copper atoms (Fe-S 0.226 nm, Cu-S 0.230 nm). The chalcopyrite structure has bond angles of 109.4° to 109.6° for the Fe tetrahedrons (S-Fe-S), and 108.68° to 111.06° for the Cu tetrahedrons (S-Cu-S). Thus, the iron tetrahedrons are very regular but the copper tetrahedrons are distorted along the z-axis (Hall and Stewart, 1973).
Klauber (2003) employed the XPS technique on fractured surfaces of chalcopyrite and showed the existence of a pyrite-like structure on the surface. His study showed that the surface structure of chalcopyrite differs from the bulk structure because of reconstruction.

The formation of this pyritic phase on the surface of chalcopyrite is associated with the chalcopyrite (001) face reconstruction to adopt a similar arrangement to the pyrite (100) face. During this reconstruction, the sulfur ions above and below the cation plane in the chalcopyrite (001) face shift 0.220 and 0.125 nm, respectively. The shift in iron atoms is minor because the surface unit dimensions for the pyrite (100) and chalcopyrite (001) faces are similar (0.542 and 0.529 nm, respectively) (Klauber, 2003).

### 2.2 Dissolution of Chalcopyrite

Several alternative mechanisms have been proposed for chalcopyrite dissolution including oxidative, reductive/oxidative and non-oxidative reactions, each of which are reviewed below.
2.2.1 Oxidative Dissolution

As explained by Nicol et al., (2010), the mixed-potential electrochemical model suggested by Jones and Peters (1976) and Miller et al. (1981) describes the oxidative dissolution of chalcopyrite in acidic ferric or cupric solutions. The dissolution occurs according to reactions (R1.1), (R1.2) and (R1.3).

In contrast to expectations that rate of dissolution increases with increasing potential at the chalcopyrite surface, the rate does not follow such a trend. It has been proposed by Dutrizac (1981) that the elemental sulfur layer formed on the chalcopyrite surface during dissolution inhibits leaching. Nevertheless, this theory is no longer accepted as the reason for chalcopyrite passivation.

Despite ongoing research in past decades to disclose the nature of this passive layer, it is still not fully understood. Previous studies have concluded that these layers can consist of impermeable sulfur formed on the surface of chalcopyrite (Dutrizac, 1978; Munoz et al., 1979), precipitated iron salts (Dutrizac, 1978), a solid electrolyte interphase (SEI) which retards the rate of charge transfer (McMillan et al., 1982), a metal deficient sulfide (Linge, 1976), a copper rich polysulfide layer formed on the surface due to solid state changes to the mineral during leaching (Hackl et al., 1995; Parker et al., 1981) or, as the most recent research has shown, it can even be two layers with different chemical compositions at different potentials growing on top of each other (Ghahremaninezhad et al., 2010).

2.2.2 Reductive/Oxidative Dissolution

Kametani and Aoki (1985) and Hiroyoshi et al. (2000 and 2001) studied the oxidative leaching of chalcopyrite with dissolved oxygen and ferric ions in sulfate media, and showed that the presence of high concentrations of ferrous ions in sulfuric acid solutions containing cupric ions increased the dissolution rate. These researchers could not use the typical oxidative model according to which the rate of copper extraction decreases (or stays unchanged) by the addition of cupric and ferrous ions to interpret their results. It is because these ions are the products of the anodic and cathodic reactions.
To explain the enhancement effect of ferrous and cupric ions on chalcopyrite leaching they proposed a two-step reaction model in which,

(1) chalcopyrite is reduced by ferrous ions to Cu$_2$S in the presence of cupric ions according to reaction:

$$\text{CuFeS}_2 + 3\text{Cu}^{2+} + 3\text{Fe}^{2+} = 2\text{Cu}_2\text{S} + 4\text{Fe}^{3+} \quad (R2.1)$$

(2) the intermediate Cu$_2$S is oxidized by ferric ions as follows:

$$2\text{Cu}_2\text{S} + 8\text{Fe}^{3+} = 4\text{Cu}^{2+} + 8\text{Fe}^{2+} + 2\text{S} \quad (R2.2)$$

According to this model, ferrous-promoted chalcopyrite leaching is in effect when the redox potential of the solution is below a calculated potential that is a function of the ferrous and cupric ion concentrations. Cu$_2$S oxidizes faster than chalcopyrite and this enhances copper dissolution in the presence of cupric and ferrous ions at low potentials (Nicol et al., 2010).

According to Nicol and Lazaro (2003), this model fails to explain how reaction (R2.1) can occur at potentials at which this process is not likely to proceed thermodynamically and kinetically. Therefore, at potentials above 0.5 V vs. SHE there is no experimental evidence to support reduction of chalcopyrite to chalcocite. Moreover, in reaction (R2.2) assuming that oxidation of Cu$_2$S proceeds through the intermediate formation of CuS, thermodynamically, it is not favorable since the equilibrium potential for the oxidation of CuS is about 70 mV more positive than that for the oxidation of Cu$_2$S. It also seems highly unlikely that Fe$^{2+}$ acts as a reducing agent simultaneously with Fe$^{3+}$ acting as an oxidant (Nicol and Lazaro, 2003).

### 2.2.3 Non-oxidative Dissolution

Under non-oxidative conditions dissolution of chalcopyrite in acidic solutions occurs according to the following reaction (Nicol and Lazaro, 2003):

$$\text{CuFeS}_2 + 4\text{H}^+ = \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{H}_2\text{S} \quad (R2.3)$$

This reaction is not thermodynamically spontaneous ($K = 2.8\times10^{-19}$ at 35°C)
Although this process was proposed by various researchers (Ammou-Chokroum et al., 1981; Dutrizac, 1990; Nicol and Lazaro, 2003; Parker et al., 1981a), the low equilibrium concentrations of the dissolved species in solution have been a practical barrier in its experimental study.

Nicol and Lazaro (2003) used the ring-disk electrode (RDE) technique to study this reaction and observed that dissolution of chalcopyrite can occur to some extent in the absence of any oxidizing agent with the formation of a detectable soluble sulfur species. They suggested a non-oxidative process based on reaction (R2.3). They proposed that the rate of reaction is controlled by two steps:

1) rapid dissolution to equilibrium at the mineral surface, and

2) diffusion of soluble products away from the chalcopyrite surface.

The maximum rate calculated, in terms of H$_2$S production, of the non-oxidative dissolution reaction was shown to approximately equal to the rate observed.

### 2.3 Oxidation and Dissolution of Pyrite

Pyrite is frequently found with valuable minerals such as chalcopyrite, sphalerite and galena. Some precious metals such as gold and silver occur in association with pyrite, but pyrite itself is not normally of economic value. Pyrite oxidation has an economic impact in industrial processes used to separate pyrite from other minerals of value such as leaching and mineral flotation (Chandra and Gerson, 2010).

Aqueous oxidation of pyrite with anthropogenic influence of mining either under natural conditions such as weathering or intentional oxidative processing such as in the hydrometallurgical treatment of copper concentrates is a ubiquitous process in the mining industry. This leads to formation of sulfuric acid and iron salts in mine drainage waters causing what is known as acid mine drainage (AMD) (Biegler and Swift, 1979a; Rimstidt and Vaughan, 2003).
Generally, sulfate and ferrous are the main products of aqueous pyrite oxidation. However, elemental sulfur, polysulfides, hydrogen sulfide, ferric hydroxide, iron oxide and iron(III) oxyhydroxide are other products of pyrite oxidation. Thiosulfate, sulfite and polythionates are also believed to be the intermediate species of pyrite oxidation. Solution potential, pH, oxidant type and concentration, hydrodynamics, grain size and surface area in relation to solution volume, temperature and pressure are the parameters affecting the oxidation and leach rates of pyrite. Of all these, solution potential is the most critical (Chandra and Gerson, 2010).

O$_2$ and Fe$^{3+}$ are the two most important oxidants for pyrite oxidation. The aqueous oxidation of pyrite is generally described by the following overall reactions (Chandra and Gerson, 2010):

\[
\begin{align*}
\ce{FeS2 + 7/2O2(aq) + H2O & -> Fe^{2+} + 2SO4^{2-} + 2H^+} \\
\ce{Fe^{2+} + 1/4O2(aq) + H^+ & -> Fe^{3+} + 1/2H2O} \\
\ce{FeS2 + 14Fe^{3+} + 8H2O & -> 15Fe^{2+} + 2SO4^{2-} + 16H^+}
\end{align*}
\]

Pyrite oxidation reactions are far from equilibrium; there is basically no reverse rate (Chandra and Gerson, 2010).

The pyrite is oxidized and the ferric and oxygen are reduced at the pyrite surface. Thus, the dissolution of pyrite is an oxidation-reduction reaction. The overall reaction can be written in terms of half-reactions as follows (Holmes and Crundwell, 2000):

\[
\begin{align*}
\ce{FeS2 + 8H2O & -> Fe^{2+} + 2SO4^{2-} + 16H^+ + 14e^-} \\
\ce{Fe^{3+} + e^- & -> Fe^{2+}} \\
\ce{O2 + 4 H^+ + 4 e^- & -> 2 H2O}
\end{align*}
\]

Reaction (R2.7) is distinct from reactions (R2.4) and (R2.6). Reaction (R2.7) is denoted as the anodic dissolution of pyrite, whereas reactions (R2.4) or (R2.6) are denoted as the oxidative dissolution of pyrite.
The rate of reactions (R2.7), (R2.8), and (R2.9) are highly dependent on the interfacial potential difference. They occur concurrently on the whole surface of the dissolving pyrite at rates which fulfill the condition of a mixed potential. Since these three reactions occur independently, each of them can be investigated separately (Holmes and Crundwell, 2000).

### 2.4 Impurities in Pyrite

In a review paper by Abraitis et al. (2004b), it is stated that pyrite samples found in nature do not have the ideal chemistry of pyrite, which is FeS$_2$. Natural pyrite usually contains small amounts of other minor and trace elements, in addition to the main elements Fe and S. It is better to categorize impurity elements into minor and trace components. The quantity of a minor element can be detected readily and it may even be up to a few percent, but is not an essential component of the mineral phase. Co, Ni and As are important examples of important trace elements in pyrite. A trace element is an element that is still detectable, although it is present in minute quantities. Atoms of a similar radius and charge or net polarity may be substituted for major mineral components, in either a stoichiometric or nonstoichiometric way. Co$^{2+}$ and Ni$^{2+}$ can substitute stoichiometrically for Fe$^{2+}$ and Se or Te can substitute for sulfur in the disulfide dianion S$_2^{2-}$. In nonstoichiometric substitutions, ions or molecular groups of differing net charge or polarity substitute for the main element. This may cause significant changes in the electrical properties of the mineral. A good example of this type in pyrite is substitution of As for S. By substituting one and two As atoms for S atoms in the disulfide dianion, because As and S have different valence numbers, AsS$^{3-}$ and As$_2$$^{4-}$ groups are formed respectively.

Bulk elemental analyses are typically not very reliable for determining impurity elements, because there may be small amounts of other minerals, present as microscopic inclusions within the pyrite matrix. Modern analytical techniques, such as electron probe microanalysis (EPMA), proton induced X-ray emission (PIXE), secondary ion mass spectroscopy (SIMS, often employing an ion microprobe) and laser ablation inductively coupled plasma mass spectroscopy (LAICP-MS), give the ability to analyze
mineral samples with high spatial resolution. Using these methods, the specimen can be imaged before a select location is analyzed on the micron scale or even smaller, thereby avoiding visible inclusions.

Khmeleva et al. (2005) used XPS to determine the surface composition of mineral particles in different phases in order to investigate the effect of galvanic interactions on the mineral surfaces. They also took advantage of ToF-SIMS since it gives the ability of specifying and imaging the sub-monolayer surface. They used the ToF-SIMS technique to study the surfaces of individual particles of chalcopyrite, sphalerite, and pyrite from concentrate and tailings samples obtained in flotation experiments.

Abraitis et al. (2004b) summarized the maximum and minimum detectable concentrations in µmol/g of minor and trace elements in pyrite as shown in Figure 2.3. Huston et al. (1995) used a proton microprobe to analyze impurity elements in pyrite. The elements were grouped into three categories: (1) elements that are present in pyrite as inclusions (Cu, Zn, Pb, Ba, Bi, Ag and Sb), (2) elements whose presence is the result of nonstoichiometric substitution in the lattice (As, Tl, Au and possibly Mo) (3) elements present as a result of stoichiometric lattice substitution for Fe (Co and Ni) or S (Se and Te). Pyrite can be cleaned of the group 1 and 2 elements by hydrothermal and metamorphic recrystallization.
Arsenic is commonly present as a minor element in pyrite although it has a limited solubility in pyrite. Arsenopyrite (FeAsS) has a marcasite crystal structure which is orthorhombic. Because pyrite and arsenopyrite have different structures, they do not form any solid solution in ore deposits. On the other hand, cobaltite (CoAsS) and gersdorffite (NiAsS) have the same structure as pyrite and can form a solid solution with it. The As present in the pyrite lattice can come from those minerals. Arsenic substitutes for sulfur in the pyrite structure and forms $\text{AsS}^{3-}$ dianions. These dianions are charge-compensated by $\text{Au}^{3+}$ in the mineral structure. Gold involves a coupled substitution mechanism, in which $\text{Au}^{3+}$ substitutes for $\text{Fe}^{2+}$ and $\text{AsS}^{3-}$ substitutes for the $\text{S}_2^{2-}$ dianion. Other trivalent metal cations such as $\text{Ti}^{3+}$ and $\text{Mo}^{3+}$ and $\text{Ag}^{3+}$ can substitute for $\text{Fe}^{2+}$ using the same mechanism.

Since $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ have similar ionic radii to $\text{Fe}^{2+}$, and both cattierite (CoS$_2$) and vaesite (NiS$_2$) adopt the pyrite structure, Co and Ni may also substitute for Fe in pyrite.
to a large extent. In ores of high-temperature origin, typically cobalt is the more abundant element. Nickel is found more in sedimentary sources.

Cu measured in pyrite may be present in two forms: microscopic inclusions of Cu-bearing mineral phases, like subsurface chalcopyrite, or in the pyrite lattice, like metastable, As-rich pyrites. Lead and zinc normally do not enter the pyrite lattice. High amounts of Pb and Zn result from galena and sphalerite inclusions within the pyrite matrix, which is generally also arsenic-rich. Se and Te enter the pyrite lattice by forming \( \text{SeS}^{2-} \) and \( \text{TeS}^{2-} \) dianions and \( \text{Se}^{2-} \) and \( \text{Te}^{2-} \) ions (Abraitis et al., 2004). Naveau et al. (2007) reported ferroselite (FeSe\(_2\)) forming on the surface of synthetic pyrite by aqueous interaction of selenium with pyrite.

According to Huston et al. (1995), silver in pyrite is due to the presence of argentiferous galena, tetrahedrite, or tennantite inclusions within the pyrite. However, the amount of Ag found in the pyrite lattice itself was less than 5 ppm. Since it has been shown by Maddox et al. (1996) that the presence of Ag has a significant effect on pyrite reactivity and Miller and Portillo (1981) also showed the effect of Ag on chalcopyrite leaching, this element deserves special attention.

### 2.5 Semiconducting Properties of Pyrite

As discussed by Vaughan and Craig (1978) pyrite is a naturally occurring semiconductor. Natural pyrite exhibits both \( n \) and \( p \)-type semiconductivity, which may even occur within the same single crystal. Jaegermann and Tributsch (1983) and Ennaoui et al. (1986) reported that natural crystals of pyrite have a bandgap energy of about 0.9 eV, while synthetic polycrystals and single crystals are more typically about 0.95 eV. Pridmore and Shuey (1976) mentioned that semiconducting properties are a result of existing free charge carriers in the crystal structure. They listed three sources for the generation of free charge carriers: (1) deviation from stoichiometric composition, (2) impurity elements in solid solution, and (3) thermal excitation across the energy gap.

In a review of the compositional, textural and electrical properties of natural pyrite, Abraitis et al. (2004b) identified a wide range of conductivities, between 0.02 and 562 (Ω
A donor defect is caused by metal excess (sulfur deficiency) and an acceptor defect is caused by metal deficiency (sulfur excess). Since defect formation requires only a small amount of energy, defects are always present. Thus, in reality, finding a perfectly stoichiometric mineral specimen is impossible. The stoichiometric deviation may be too small to be detected by chemical analysis, while at the same time, large enough to cause observed electrical charge carriers.

Impurity atoms in solid solution normally influence semiconducting properties in the following ways: if an element substituting for Fe or S is to the right of Fe or S, respectively, on the periodic table, it forms a donor defect. Conversely, if an element substitutes from the left, it forms an acceptor defect. Substitution from the same group, for example Se for S, has no effect other than a reduction in mobility. A metal interstitial is a donor, and anion interstitials are generally not present in significant quantities.

In the 1970s it was concluded that the electronic conduction properties of minerals do not influence the hydrometallurgical oxidation and dissolution reactions (Springer, 1970). Biegler (1976) similarly pointed out that there is no explicit correlation between the kinetics of oxygen reduction and the semiconducting properties of pyrite. However, it was shown by researchers (Mishra & Osseo-Asare, 1988; Mishra & Osseo-Asare, 1992; Osseo-Asare, 1993) that the electrochemical behavior of pyrite is influenced by its semiconducting properties.

The electrochemical dissolution of semiconductors can occur by electron movement to the surface to reside in cationic surface states. They interface with the bond between the cation of the semiconductor and the neighboring anion, or with holes which have moved to the surface in anionic surface states, thereby eliminating the bonding electron.
Gerischer (1981) suggests that oxidative decomposition of a semiconductor is caused by reactions with holes and reductive decomposition by reactions with electrons. Electrons and holes may be involved in different steps of the overall reaction. Shuey (1975) determined that electron mobility in pyrite is about two orders of magnitudes greater than hole mobility. According to Gerischer (1981), considering MA as a binary-compound semiconductor, two different reactions can be written as follows:

\[
\text{MA} + (z - x)h^+ + \text{solv} \rightarrow M^{z^+}.\text{solv} + A + xe^- \quad p_{E_d} \\
\text{MA} + (z - y)e^- + \text{solv} \rightarrow M + A^{2^-}.\text{solv} + yh^+ \quad n_{E_d}
\]

(R2.10) (R2.11)

If the band gap is greater than 1 eV then \(x\) and \(y\) become zero. \(p_{E_d}\) and \(n_{E_d}\) are equilibrium potentials for the above reactions; \(n\) and \(p\) denote decomposition by electrons or holes. Gerischer (1981) states that decomposition occurs either when the redox potential of holes is more positive than the anodic decomposition potential \((p_{E_d})\) or when the redox potential of electrons is more negative than the cathodic decomposition potential \((n_{E_d})\). The thermodynamic criterion for these reactions to proceed is that the electrochemical potential, \(E\), must be greater than the equilibrium potentials.

The free energies of electrons and holes are only equal under equilibrium conditions. Under nonequilibrium conditions, the Fermi level energies for electrons and holes are given by:

\[
p_{E_f}^* = E_v - kTln\left(\frac{p^*}{N_v - p^*}\right) \quad (2.1)\\n\]

\[
n_{E_f}^* = E_c + kTln\left(\frac{n^*}{N_c - n^*}\right) \quad (2.2)
\]

where,

\(E_c\) and \(E_v\) = energy position of conduction and valence band (eV)

\(p^*\) and \(n^*\) = nonequilibrium concentration of electrons and holes (cm\(^{-3}\))

\(N_v\) and \(N_c\) = effective density of states of electrons and holes in valence and conduction bands (cm\(^{-3}\))

As discussed by Osseo-Asare (1992), an electrochemical reaction at the semiconductor-electrolyte interface involves interfacial charge transfer. Charge transfer
occurs when the level of the aqueous species fluctuates to the same energy as the conduction or valence band in the solid. Charge transfer occurs by alignment of energy levels in the semiconductor and electrolyte. Therefore, by comparing the energy levels of the redox couple \((E_{\text{red}}, E_{\text{ox}})\) with energy bands of the semiconductor \((E_c, E_v)\), the probability of charge transfer can be assured.

Charge can be transferred through the conduction band or the valence band and it occurs through whichever band is closer to \(E_{\text{redox}}\). When the surface of a semiconductor is brought into contact with an aqueous solution, and if the redox potential of the solution and the Fermi level do not lie at the same energy, there will be a transfer of electrons or holes between the energy bands of the semiconductor and the aqueous solution to equilibrate the two phases. The Fermi level is defined as the energy level at which the probability of occupation by an electron is 1/2 and represents the electrochemical potential of an electron in a material. As has been discussed by Nozik and Memming (1996), the semiconductor solid-state physics community has adopted the electron energy in vacuum as a reference, whereas electrochemists use the standard hydrogen electrode (SHE) scale as the reference. In order to calculate the energy of a redox couple in an absolute energy scale equation (2.3) can be used. It is also depicted in Figure 2.4a.

\[
E_{F,\text{redox}} = -4.5 \, eV - eE_{\text{redox}}
\]  

(2.3)
Figure 2.4  (a) Left-hand side shows the energy levels in a semiconductor and right-hand side shows energy distribution of the occupied and unoccupied states of the redox acceptor. $\chi$ is the semiconductor electron affinity and $\phi$ is the work function. (b) and (c) show the semiconductor-electrolyte interface before and after equilibration with redox species, for $n$-type and $p$-type semiconductors, respectively (adapted from Nozik & Memming, 1996).

Osseo-Asare (1992) explains that the excess charge that is spread on the semiconductor after equilibration does not reside at the surface, but extends into the electrode for a significant distance in the range of 100 to 10,000 Å. This region is called the space charge region. Figure 2.4b and c depict the semiconductor-electrolyte
interface before and after equilibration for $n$-type and $p$-type semiconductors, respectively. Rajeshwar (2003) distinguishes the behavior of a metal electrode from a semiconductor electrode in an electrolyte by pointing at the differences in charge accumulation on their surfaces. Since metals have high electronic conductivity, they cannot support internal electric fields. Thus the charge, and consequently the associated potential drop, is concentrated at the surface penetrating at most a few angstroms.

When a metal electrode is in contact with an electrolyte, the potential drop at the interface occurs within the Helmholtz region on the electrolyte side. But when a semiconductor is in contact with an electrolyte, the interfacial potential drop appears in two parts, across both the space charge and Helmholtz regions ($V_{SC}$ and $V_{H}$), which can be modeled as a simple equivalent circuit consisting of two capacitors $C_{SC}$ and $C_{H}$ in series. This is depicted in Figure 2.5.

Figure 2.4 depicts reorganization energy, $\lambda$, which was introduced by Marcus (1965) as the energy required during the electron transfer process, without changing the electronic state. Reorganization energy, as explained by Schmickler and Frank (2003), plays an important role in the Marcus theory of electron transfer. It is usually treated as the sum of two contributions: one from the surrounding solvent which is called outer-sphere reorganization ($\lambda_{out}$) and the other arising from changes in the bond lengths and vibration frequencies of the reacting complex itself ($\lambda_{in}$) which is called inner-sphere reorganization. In other words, $\lambda$ can be described as the energy associated with the change in the internal structure of the oxidized ion and the change in solvation as the ion goes through the reduction process to the reduced ion.
Gerischer (1991) used a Gaussian-type distribution to describe the energy distribution of a redox couple which may be caused by the thermal fluctuation model. The distribution functions for the states are given by equations below:

\[
D_\text{ox} = \exp \left( -\frac{(E-E_{F,\text{redox}}-\lambda)^2}{4k_B T \lambda} \right) 
\]

(2.4)

\[
D_\text{red} = \exp \left( -\frac{(E-E_{F,\text{redox}}+\lambda)^2}{4k_B T \lambda} \right) 
\]

(2.5)

When ions react with polarized water molecules, it changes the orbital energy levels. This effect is reflected in the probability distribution.

In order to construct an energy model for the semiconductor-electrolyte interface, knowledge of the flat band potential is essential. Flat band potential can be used to locate the energy levels of the semiconductor and compare semiconductors as well as
the energy levels of the redox couple existing in the solution. Following such a comparison, the electron transfer mechanism at the interface can be predicted and interpreted, or for a specific application the right semiconductor electrode can be selected (Lemasson et al., 1981).

Gelderman et al. (2006) defines flat band potential as follows: when a semiconductor electrode with \( E_F \) greater than \( E_{F,\text{redox}} \) comes into contact with an electrolyte, equilibrium is achieved through the transfer of electrons from the semiconductor to the oxidant so the Fermi levels for both phases become equal. As a result, the semiconductor will be charged positively, and there will be a diffuse charge in the semiconductor which is counterbalanced by a layer of charge on the electrolyte side. By manually changing the voltage of the semiconductor using a potentiostat, the level of band bending can be changed. At a certain applied voltage there is no band bending or charge depletion. This voltage is called the flat-band potential (\( V_{fb} \)) of the semiconductor. The effect of applied potential is depicted in Figure 2.6.
Lehner et al. (2006) measured the semiconducting properties of synthetic pyrite doped with As, Ni and Co using a van der Pauw measurement system (van der Pauw, 1958). Their measurements showed important differences in the electrical properties of pyrite when As, Co or Ni are present as minor elements. When Co is present as a minor element it raises carrier concentration and mobility in pyrite thus resulting in a higher conductivity by five orders of magnitude, as compared with undoped pyrite. Ni has an effect of increasing mobility but no effect on the carrier concentration. Thus it raises the conductivity by one order of magnitude over undoped pyrite. Arsenic increases the carrier concentration and decreases the mobility, resulting in slightly higher conductivity than undoped pyrite. Pyrite doped with As shows $p$-type behavior but pyrite doped with Co and Ni show $n$-type behavior.
Lehner et al. (2007) measured several parameters such as the cyclic voltammetry current peak generated from the ferric reduction reaction, the amplitude of the AC voltammetry peak from the ferric reduction reaction, and the current generated from the anodic dissolution of pyrite at a certain potential in order to relate the impurity concentrations to the bulk electrical properties. They presented evidence for a higher oxidation rate for pyrite with arsenic as a dopant compared to the other types. This is shown in the anodic branch of polarization curves generated from their experiments.

Based on the anodic Tafel slopes given by:

\[
\text{Oxidation slope} = \frac{(1-\alpha)F}{2.3RT}
\]  

(2.6)

The average value of the transfer coefficient was calculated. The calculated value of \( \alpha \) is 0.57. Their results show that the current density increases with an increase in arsenic concentration.

2.5.1 Evidence for the Effect of Surface States on Reactivity of Pyrite

Lehner et al. (2007) related the reactivity to surface states using evidence from electrochemical etching of the electrode. In their experiments those pyrite electrodes that were electrochemically etched before the cyclic voltammetry test showed a quasi-reversible reaction with ferric iron in solution. They did not observe any response from those samples that were not etched beforehand. The etching procedure consisted of anodic dissolution using a cyclic voltammetry sweep. After that, in the return cathodic scan, the ferric iron reduction peak can be seen around 0.44 V. The increase in ferric reduction might be due to specific reaction sites such as kinks and steps which emerged during electrochemical etching and from an increased number of defects, resulting in a higher density of surface states and electrons within the band gap. The increase from 0.2 to 0.5 of the transfer coefficient \( \alpha \) which was measured from cathodic Tafel slopes before and after anodic dissolution represents a change in the surface. The possibility of removal of a charge transfer-inhibiting oxide coating during the etching procedure may also be valid since Lehner et al. (2007) did not give any evidence to reject this hypothesis.
2.6 Gold and Silver Nanoparticles

The modification of electrodes with metallic nanoparticles, to enhance the electrode properties is a prevalent technique used by electrochemists these days. The layers of nanoparticles give rise to a porous, high surface area electrode. The catalytic properties of metal nanoparticles could reduce the required over potentials for some important electrochemical reactions and even provide electrochemical reversibility for redox reactions, which are irreversible at bulk material electrodes (Katz et al., 2004).

Michael Faraday presented the first scientific description of the properties of nanoparticles in his classic paper “Experimental relations of gold (and other metals) to light” (Faraday, 1857).

In recent years, considerable attention has been focused on the synthesis and study of metal nanoparticles due to their potential applications in the fields of physics, chemistry, biology, medicine, material science and their interdisciplinary fields (Balan et al., 2005).

When material is nano-sized, the physical properties deviate markedly from those of bulk material; however, this effect is highly dependent on the particle size, interparticle distance, and morphology of the nanoparticles (Daniel and Astruc, 2004).

An extremely small region of space defined in a semiconductor material on the order of nanometers is called a quantum dot, a term coined by Reed (1993). The three dimensional confinement of quantum dots can change properties of the excitons in comparison to free excitons in a bulk material (Gywat et al., 2010). Nanoparticles behave electronically as zero-dimensional (restricted in all three dimensions) quantum dots when the de Broglie wavelength of the valence electrons and the particle are in the same size range.

As Reed (1993) explains, electrons confined in a plane have no freedom to move in the third dimension. Those confined in a quantum wire are only free to move in one dimension, and those confined in a quantum dot are not free to move in any dimension. An electron inside a cube of material 10 nm on a side is effectively confined to a point.
Quantum dots have now become commonplace as was the case for the quantum wells and hills in the early nineties. Reed (1993) describes quantum wells as semiconductors that were built up one atomic layer at a time, which attract electrons. The energy of these electrons within the well is lower than the energy of those outside, thus the electrons flow in, just as water moves downhill from one place to another. As it was possible to confine electrons to a plane it is possible to confine them to a point. Gold quantum dots were reported by Zheng et al. (2004), and were highlighted on the cover of the same issue of *Physical Review Letters*.

It has been a high priority in semiconductor physics to design and manufacture artificial structures in which the electrons can be confined in zero, one, and two dimensions (Racec et al., 2003). The physics of quantum dots can be studied by measuring their transport properties, or in other words, by their ability to carry an electric current (Kouwenhoven et al., 1997). Tunneling is the most studied transport phenomenon associated with quantum transmission. The term tunneling is used when a particle transports through a classically forbidden potential region (Figure 2.7). Recalling the Schrödinger wave equation, the square of the wave function represents the probability density for finding a particle within a given region of space. Thus, quantum-mechanically, an electron incident on a potential barrier has a finite probability of tunneling through the barrier and appearing on the other side (Ferry et al., 2009).

![Figure 2.7](image)

Figure 2.7  Schematic illustration of quantum mechanical tunneling through a potential barrier. The points A and B represent the classical turning points (adapted from Ferry et al., 2009).
Nanoparticles can be broadly categorized into two classes: organic and inorganic nanoparticles. Carbon based materials such as fullerenes and carbon nanotubes are examples of organic nanoparticles. Nanoparticles based on metal oxides (zinc oxide, iron oxide, titanium dioxide and cerium oxide etc.), and noble metals (gold and silver) are examples of inorganic nanoparticles. There are two approaches to manufacturing nanoparticles: The “top-down” approach involves breaking down bulk material to generate the required nanostructures. The “Bottom-up” approach involves assembling single atoms and molecules into larger nanostructures linked with chemical reactions, nucleation and growth processes. Synthesis of nanoparticles can be carried out by physical or chemical methods (Ju-Nam and Lead, 2008).

Citrate reduction of HAuCl₄ in water has been the most common method of synthesis of Au nanoparticles by reduction of Au(III) since its introduction by Turkevitch et al. (1951). Frens (1973) expanded this method by varying the ratio of trisodium citrate to gold to generate Au nanoparticles of predetermined size (between 16 and 147 nm). A similar procedure can be applied to reduce silver salts, although particle size control is not as easy as it is for Au nanoparticles (Marzan, 2002).

Another procedure is a two-phase method known as the Brust-Shiffrin method (Brust et al., 1994). In this method HAuCl₄ is dissolved in water and subsequently transported into toluene by a phase transfer agent (tetraoctylammonium bromide). Subsequently, the toluene solution is mixed and stirred with an aqueous solution of sodium borohydride, in the presence of thioalkanes or aminoalkanes (Marzan, 2002).

A simple method to synthesize optically controllable gold-coated nanoparticles with a nonmetallic core, was introduced by Zhou et al. (1994). In their two-step method, solid chloroauric acid (HAuCl₄.4H₂O) and sodium sulfide (Na₂S.9H₂O) were dissolved in pure water at room temperature and controlled amounts of the two solutions were mixed to get an unstable gold sulfide Au₂S. In the second step, a small amount of Na₂S solution was injected into the Au₂S solution. They interpret that at later times in the reaction; S₂²⁻ diffuses through the gold shell and reduces the Au₂S core. Thus, the shell
thickness increases and consequently the core becomes smaller until the particles become pure gold.

Averitt et al. (1997) challenged this idea by pointing out that S\textsubscript{2}\textsuperscript{2−} is not the dominant aqueous species in solution at any pH. They claimed based on their understanding of the optical properties of Au that nanoshells grow according to a two-stage model where first the Au\textsubscript{2}S core, and then the Au shell, grows linearly in time.

When Na\textsubscript{2}S is mixed with water at pH 7, the S\textsubscript{2}\textsuperscript{2−} reacts with water and gives HS\textsuperscript{−} and OH\textsuperscript{−}. Therefore, the initial reactants are AuCl\textsubscript{4}− and HS\textsuperscript{−}. Averitt et al. (1997) proposed the following reaction for the growth of Au coated Au\textsubscript{2}S nanoparticles:

\[
2\text{AuCl}_4^- + 3\text{HS}^- = 2\text{Au} + 3\text{S} + 3\text{H}^+ + 8\text{Cl}^-
\]  

(R2.12)

Based on the above reaction Au and S are available for subsequent nucleation and growth and both Au and Au-coated Au\textsubscript{2}S nanoparticles are grown simultaneously.

Although colloid chemistry is a well established method for producing gold nanoparticles with a narrow size distribution, there are physical methods as well. The oldest reference using a physical method was introduced by Faraday (1857) which involved electrical explosion of a gold wire in different atmospheres and collection of the particles on various substrates. In modern methods low-pressure evaporation and subsequent condensation in a stream of inert gas have been used. At atmospheric pressure, to achieve a high rate of evaporation below the melting point, gold mesh or gold-covered tungsten wire have also been used. Another method involves producing gold aerosols using the evaporation/condensation technique with pure molten gold as source material and reshaping particles to spheres at temperatures above the melting point resulting in classified particles according to their size (Magnusson et al., 1999).

2.6.1 Characterization of Gold and Silver Nanoparticles

Transmission electron microscopy (TEM) is the standard technique employed for finding precise data about the average size and size distribution of noble metal nanoparticles. However, there are some disadvantages in using TEM; it does not allow fast and simple
monitoring of nanoparticle size and it does not provide any data about nanoparticle aggregation and concentration. Moreover, TEM sample preparation is difficult and nanoparticle size distribution and morphology may be altered during sample preparation. Conversely, UV-Vis spectroscopy is a more readily available, non-destructive, rapid, bulk analytical technique (Amendola and Meneghetti, 2009).

Other methods such as scanning tunneling microscopy (STM), atomic force microscopy (AFM), small-angle X-ray scattering (SAXS), laser desorption-ionization and mass spectrometry (LDI-MS) and X-ray diffraction have also been used to characterize Au nanoparticles (Daniel and Astruc, 2004). These analysis methods are even more expensive or less accessible than TEM.

Freely mobile electrons become trapped in quantum dots and show a characteristic collective oscillation frequency of the resonating plasma (resonating here means a condition in which the frequencies and wave vectors of both incident and surface plasmon waves are approximately the same, resulting in a constructive interference and eventually a stronger signal), generating what is known as a plasmon resonance band (PRB), observed at about 530 nm wavelength in the gold particles with a diameter of 5 to 20 nm (Daniel and Astruc, 2004). For metallic nanoparticles it is denoted as localized surface plasmon (LSP). Excitation of LSPs by light, at a wavelength where resonance occurs, generates SP absorption bands. The intensity and frequency of the SP absorption bands (i.e., color) are characteristic of each material (viz. gold and silver) and are very sensitive to the size, size distribution, morphology, the nature of the nanoparticle-matrix interface, and the dielectric properties of the surrounding matrix. The red color of an aqueous dispersion of colloidal gold particles is due to the LSPR (localized surface plasmon resonance) (Hutter and Fendler, 2004). Figure 2.8 illustrates the conduction electrons of a spherical gold colloid oscillating coherently in response to the electric field of incident light.
The physical phenomenon of metal nanoparticles surface plasmon resonance has found large applications for chemical and biological sensing, due to their sensitive spectral response to local surface environment and ease of monitoring. The gold and silver systems are unique in that their densities of free electrons are in the proper range to give their nanoparticles SP peaks in the visible region (Xia and Halas, 2005).

Dependence of LSPR on nanoparticles size and shape, deems UV-Vis spectroscopy a suitable technique for characterization of the colloidal solutions by fitting the spectra with the Mie model for compact spheres and the Gans model for spheroids (Amendola et al., 2006).

Using a Mie-Gans fitting model for UV-Vis experimental data, the following parameters can be calculated: (i) average radius of the nanoparticles ($R$); (ii) the standard deviation ($\sigma_G$) of the a/b Gaussian distribution; (iii) the fraction of spherical to spheroidal of nanoparticles (Amendola, 2008).
CHAPTER 3: Experimental and Instrumental

3.1 Material

Five different concentrates were used in this research; a chalcopyrite concentrate containing 92% chalcopyrite, and four pyrite samples containing 92.3 %, 80.4%, 97.6% and 92.7 % pyrite, from various sources. Mineralogical and elemental compositions of the copper concentrate and pyrite samples are summarized in Table 3.1 and Table 3.2, respectively.

Table 3.1 Quantitative XRD analysis of mineral abundance in copper and pyrite concentrates (all values in wt%).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Cu Conc</th>
<th>Pyrite #1</th>
<th>Pyrite #2</th>
<th>Pyrite #3</th>
<th>Pyrite #4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>3.7</td>
<td>92.3</td>
<td>80.4</td>
<td>97.6</td>
<td>92.7</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>MoS₂</td>
<td>0.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>2.2</td>
<td>0.8</td>
<td>1.3</td>
<td>0.6</td>
<td>1.3</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
<td>92</td>
<td>—</td>
<td>3.8</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg₃Si₄O₁₀(OH)₂</td>
<td>0.8</td>
<td>0.9</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Fluorite</td>
<td>CaF₂</td>
<td>—</td>
<td>4.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>(Zn,Fe)S</td>
<td>—</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Marcasite</td>
<td>FeS₂</td>
<td>—</td>
<td>0.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>CaSO₄</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.8</td>
<td>—</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
<td>—</td>
<td>—</td>
<td>9.2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Fe₁₋ₓS</td>
<td>—</td>
<td>—</td>
<td>2.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Clinohlore</td>
<td>(Mg,Fe²⁺)₂Al(Si₃Al)O₁₀(OH)₆</td>
<td>—</td>
<td>—</td>
<td>0.9</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₂AlSi₃O₁₀(OH)₂</td>
<td>—</td>
<td>—</td>
<td>0.2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.6</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>Al₂Si₄O₁₀(OH)₂</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Biotite</td>
<td>K(Mg,Fe)₃(AlSi₃O₁₀)(OH)₂</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.8</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>2.6</td>
</tr>
</tbody>
</table>
Table 3.2 Elemental composition of chalcopyrite and pyrite concentrates, all the values are in wt% unless otherwise noted.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu conc</th>
<th>Pyrite #1</th>
<th>Pyrite #2</th>
<th>Pyrite #3</th>
<th>Pyrite #4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>31</td>
<td>0.35</td>
<td>1.7</td>
<td>0.13</td>
<td>11 ppm</td>
</tr>
<tr>
<td>Fe</td>
<td>30</td>
<td>43.5</td>
<td>41.49</td>
<td>45.43</td>
<td>47.45</td>
</tr>
<tr>
<td>Mo</td>
<td>0.24</td>
<td>—</td>
<td>7 ppm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ca</td>
<td>0.01</td>
<td>0.17</td>
<td>2.09</td>
<td>0.56</td>
<td>—</td>
</tr>
<tr>
<td>Mg</td>
<td>0.16</td>
<td>0.03</td>
<td>0.82</td>
<td>0.04</td>
<td>—</td>
</tr>
<tr>
<td>Zn</td>
<td>—</td>
<td>0.8</td>
<td>324 ppm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pb</td>
<td>—</td>
<td>0.4</td>
<td>44 ppm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>W</td>
<td>—</td>
<td>0.12</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Bi</td>
<td>—</td>
<td>0.11</td>
<td>—</td>
<td>—</td>
<td>201 ppm</td>
</tr>
<tr>
<td>Cr</td>
<td>—</td>
<td>212 ppm</td>
<td>—</td>
<td>—</td>
<td>9 ppm</td>
</tr>
<tr>
<td>As</td>
<td>20 ppm</td>
<td>356 ppm</td>
<td>61 ppm</td>
<td>—</td>
<td>11 ppm</td>
</tr>
<tr>
<td>Ag</td>
<td>5 ppm</td>
<td>225 ppm</td>
<td>&lt;5 ppm</td>
<td>21 ppm</td>
<td>—</td>
</tr>
</tbody>
</table>

3.2 Atmospheric Leaching Experiment

Batch leaching tests were carried out in a sealed, jacketed, 2.7 L glass reactor as shown in Figure 3.1. The reactor was maintained at the desired temperature with a circulating hot water bath. The temperature, potential and pH were monitored by three probes inserted into the reactor and connected to a multi-channel digital controller (ADI 1030 Bio-Controller). The outputs of the three electrodes were recorded by a computer. The controller allowed a redox potential set point to be specified. By sending an analog signal to a gas mass flow valve, the redox potential measured by the electrode inside the reactor was controlled by the oxygen flow rate to maintain the set point. This valve controlled the oxygen flow into the reactor via a sparger from a compressed gas cylinder. The reactor was filled with 1500 g of DI water and the desired mass of sulfuric acid to make up a 0.5 M solution. Prior to use, the redox probe and pH probes were checked and calibrated. Ferric and ferrous sulfate salts were added to set a potential for the solution upon reaching 80°C. The oxygen flow from a compressed gas cylinder
controlled by a multi-channel digital controller reset the potential whenever it fell below the set point.

When the solution reached the desired temperature, the concentrate was introduced to the reactor and the stirring speed was increased to 1200 rpm. Samples for analyzing the amount of dissolved copper were withdrawn from the reactor periodically using a syringe. Leachate solutions were analyzed for copper by atomic absorption spectrometry (Varian AA240), and solid samples by induction coupled plasma (ICP) spectroscopy. For a more detailed explanation of this method and the Galvanox™ process in general, readers are referred to the paper by Dixon et al. (2008).

The electrochemical behavior of chalcopyrite was investigated during leaching in both the presence and absence of pyrite. An experiment containing pyrite was conducted under otherwise identical conditions as given above. As analysis was desired on chalcopyrite alone once the leach was completed, a series of preparation and separation techniques was employed to eliminate pyrite from the final solid sample. Initially the chalcopyrite and pyrite were ground to different particle sizes. P80 values (80% mass-passing sizes) of 75 μm for chalcopyrite and 300 μm for pyrite #1 and pyrite #2 were obtained. After leaching, samples were separated by a three-step process, beginning with vacuum filtration to separate the solid and liquid phases, followed by wet sieving to obtain an adequate degree of separation between size fractions. A water spray nozzle located above the uppermost sieve was employed to rinse samples until the liquid leaving the sieve stack was no longer turbid with solid particles. Finally, dry sieving was used after the samples were air-dried in room temperature overnight. In this step, sieving was conducted manually; each sieve was shaken over a clean tray for no less than three minutes.

In order to prepare samples for micro Raman spectroscopy, solid-liquid separation was achieved via vacuum filtration. Leachate solutions were used for chemical analysis to measure the amount of copper extracted. Separated solid samples were stored in the dark, at 25°C and under argon in a sealed desiccator to prevent further reaction before micro Raman spectroscopy analyses were conducted.
3.3 Electrochemical Techniques

3.3.1 Macro Electrode

Macro electrodes were prepared by cutting the natural mineral samples into cubic shapes to give a working surface of approximately of 1 cm² exposed to the electrolyte. The mineral sample was connected to a copper wire the back of the sample with silver-loaded epoxy resin (Mg Chemicals). The electrode contacts were isolated from the liquid medium by mounting the whole assembly in epoxy resin matrix (LECO), leaving only one face of the electrode exposed to the electrolyte. After sectioning the minerals using a precision saw, in order to remove the rough surface of the mineral samples; they were first ground using rotating discs covered with silicon carbide paper and water. The grinding was then continued with successively finer grained silicon carbide papers.
Then they were polished using rotating discs covered with soft cloth impregnated with alumina suspended in solution in order to remove the surface defects. Once the polishing was completed (this took from 30 seconds to several minutes depending upon the state of the electrode), the electrode surface was rinsed completely by spraying DI water to remove all traces of the alumina particles. At the end the electrodes were sonicated in DI water for a few minutes to remove residual abrasive particles completely. These two last steps in the preparation protocol were of vital importance since the presence of alumina particles on the surface of working electrode can affect the electron transfer kinetics. Figure 3.2 depicts a schematic illustration of a macro electrode.

![Figure 3.2 Schematic illustration of a macro electrode.](image-url)
3.3.2 Carbon Paste Electroactive Electrode (CPEE)

3.3.2.1 Background

Generally, most fundamental electrochemical studies of sulfide mineral processes use natural solid crystal mineral samples of high purity as the working electrode. These sulfide samples are usually museum samples or have been sampled from locations where specimens are found in a massive form. The main problem with these working electrodes is that they do not correspond to the ground sulfide mineral particles found in leaching operations.

Furthermore, compositional variations have a major impact on the semiconductive and dissolution behavior of sulfide minerals. Thus, it is necessary to develop techniques to study the fundamental electrochemical behavior of sulfide particles from actual leaching operations.

Carbon Paste Electroactive Electrodes (CPEE) were first introduced in the 1950s for analytical purposes, specifically in anodic polarography (Adams, 1958). CPEE have previously been applied to the electrochemical study of sulfide minerals by Gerlach and Kuezecci (1983), Kuezecci and Kammel (1988), Ahlberg and Åsbjörnsson (1993), Lazaro et al. (1995) and Lu et al. (2000). Cruz et al. (2005) and Urbano et al. (2007) used CPEE as a new experimental strategy to determine the galvanic interactions between sulfide mineral concentrates as an alternative to other methods such as using short-circuited galvanic cells with the dissimilar mineral electrodes connected by a wire (Mehta and Murr, 1983; Nowak et al., 1984) or powdered ore sample mixed and pressed under high pressures to put them in physical contact (Madhuchhanda et al., 2000; Paramguru and Nayak, 1996). Cruz et al. (2005) applied this strategy to simulate the conditions under which industrial leaching of sulfide minerals takes place. However, CPEE have some inherent problems, such as: limited lifetime due to the oxidation of the samples in the presence of the electrolytic binder, deterioration caused by the silicone oil binder, and affected response and performance of the electrode caused by the binder viscosity.
3.3.2.2 Preparation of Carbon Paste Electroactive Electrodes (CPEE)

The Carbon Paste Electroactive Electrodes (CPEE) were made by mixing 0.4 g of graphite (Fisher grade 38) with 0.6 g of electroactive mineral. After mixing the electroactive mineral and graphite, 0.6 mL of silicone oil (Aldrich) was added as a nonconducting binder. Other proportions for the recipe were also used by the authors, but the aforementioned mixture was used in the majority of tests. The resulting homogeneous paste was placed in a 5 mL plastic syringe and pushed out of the tube with the plunger in order to renew the surface after each experiment. The surface area measured 0.0314 cm$^2$. A platinum wire was immersed in the paste to conduct the electricity to the potentiostat. For further details about these electrodes the reader is referred to work published by Lazaro et al. (1995). A CPEE prepared from chalcopyrite ground mineral is shown in Figure 3.3.

![Figure 3.3 A carbon paste chalcopyrite electrode with non-conducting binder.](image)
3.3.3 Solid Paraffin Carbon Paste Electrode (SPCPE)

3.3.3.1 Background

As an alternative to CPEE, mechanically immobilized solid particles at the surface of graphite rods impregnated with paraffin, introduced by Scholz et al. (1989), for voltammetry of microparticles was used. However, while this type of electrode permits the direct analysis of solid ground samples, it also suffers from several drawbacks. Particles occluded by paraffin during preparation of the electrode render it unreliable for quantitative analysis.

A new methodology was introduced by Almeida and Giannetti (2002) in order to permit direct electrochemical analysis of ground mineral particles. In this method, two types of electrodes are combined; the CPEE and mechanically immobilized solid particles on carbon surfaces. This method shows good versatility. It avoids the use of binders or other agents in order to overcome major deterioration problems. It is inexpensive and easy to prepare and modify. It can be used in a wide potential window and offers excellent electrical conductivity.

3.3.3.2 Preparation of Solid Paraffin Carbon Paste Electrodes (SPCPE)

This type of electrode was made using a modified version of the method of Almeida and Giannetti (2002). A copper rod, 6.4 mm in diameter, was dipped in a mixture of 2 g of graphite and 2.4 g of paraffin wax and heated up to 70°C. About 3 to 4 g of powdered mineral were placed in a weigh boat, and the hot coated rod was pressed onto the mineral particles. The perimeter of the electrode was cut using a knife, so that the covered area of the electrode would match the area of the copper rod. The result was a disk made of ground mineral with a diameter of 6.4 mm. The side of the electrode was then wrapped in Teflon tape to prevent it from interacting with the electrolyte. The resulting mechanically immobilized particles were quite firmly attached to the graphite/paraffin mixture, which allowed the electrodes to be washed before placing in the cell.
The exposed surface of the working electrode was circular and planar with a geometrical surface area of approximately 0.316 cm$^2$. In order to measure the accurate surface area of electrodes, photomicrographs were prepared using a light microscope and then measured using Image J freeware (Image J). Geometrical surface area was used in calculation of current densities. Due to the rough nature of the powder specimen, the actual surface area was larger than the geometrical surface area. This gave greater current densities from electrodes prepared from mineral powders than from those prepared from polished mineral specimens.

The particle size distribution of the electroactive mineral has a major impact on the surface area of the electrode and must be considered during electrode preparation.

### 3.3.4 Electrochemical Cell

The experiments were conducted in a three-electrode cell with an electrolyte volume of 1 L. All the experiments were performed using a stationary electrode and a computerized potentiostat/galvanostat (EG&G PARSTAT 2273), and were conducted at room temperature. All solutions were prepared in DI water. All chemicals were of reagent grade and were used without further purification. The electrolyte consisted of 0.5 M sulfuric acid. High purity argon gas was used to remove dissolved oxygen by dispersion through a coarsely porous sintered glass disk in the stirred solutions. All solutions were purged for twenty minutes before immersion of the electrode. The solutions were stirred at 500 rpm with a 3.5-cm Teflon-covered magnetic stirring bar during gas purging, but were not stirred during the actual experiments.

The reference electrode was a large saturated calomel electrode (SCE). All the measured potentials in this thesis are versus SCE, or +242 mV vs. the standard hydrogen electrode (SHE). The counter electrode was a graphite rod 20 cm long and 0.6 cm in diameter.
3.3.5 Single Particle Micro Electrode Technique

One of the disadvantages of conventional EIS is that it does not consider reactions occurring at specific sites; it only measures average values across the surface of the electrode. When it comes to investigating the electrocatalytic activity of materials, this drawback is pronounced when neglecting the influence of lattice imperfections such as kinks, different doping elements and local variations in mineral composition. Several attempts have already been made to detect defects by localized impedance spectroscopy.

This study adopts a technique developed to study fundamental electrochemical interactions of individual particles measuring less than 100 microns in diameter.

Microelectrode techniques have shown versatility in kinetic studies of electrochemical reactions. Many of the undesirable aspects of conventional electrochemical and electroanalytical techniques can be reduced or eliminated with microelectrodes. Some of their advantages can be attributed to: ease of measurement of very small currents (rates of reaction), high rates of diffusion flux, less interference by resistive polarization and capacitive charging currents due to the double-layer capacity and small IR losses in solution. These excellent properties cause microelectrodes to exhibit superior signal-to-noise characteristics, which make them suitable for measurements of small environments such as biological cells. These exceptional properties of microelectrodes not only greatly improve the quality of experimental data, but also allow electrochemical measurements to be based on sound fundamental principles and facilitate measurements on novel systems which would not be amenable otherwise to conventional electroanalysis methods (Fleischmann and Pons, 1987; Montenegro et al., 1991; Uchida et al., 1997).

Gaining insight into the intrinsic characteristics of sulfide minerals is easier by isolating the target particles from the complex mixture of particles found in the concentrate. This technique not only obtains more localized information but also eliminates potential interference from binders and other additives used in carbon paste electrode methods. The most relevant studies using individual micron-size particles focus on battery active
material including transition metal oxides in non aqueous electrolytes. In this field, important pioneering work has been done by Uchida et al. (1997).

Single-particle microelectrodes made from sulfide mineral particles enable researchers to investigate the electrochemical and semiconducting properties of ground particles of concentrates in leaching tanks. This method has been used before for cyclic voltammetry investigation of sulfide minerals (Rivera-Vásquez, 2010; Vermaak et al., 2006).

Typically, in preparation of microelectrodes, noble metals are used. Tungsten or carbon fibers can be used too. The tips of the microelectrodes are usually insulated by glass, resin, electrophoretic paint or other organic coatings, leaving only the sharpest point of the tip uncovered, in order to reduce the electroactive area of the microelectrode (Pernkopf et al., 2005).

To date, there is little literature available on applying microelectrodes in EIS studies of minerals. Overlapping of different processes occurring at the surface of substrate and the specific properties of the microelectrodes have made the interpretation of impedance data challenging (Pernkopf et al., 2005). In this study, microelectrodes are applied for CV and EIS measurements.

### 3.3.5.1 Microelectrode Preparation

Micropipettes were pulled from 1.2 mm OD, 0.68 mm ID borosilicate capillary tubing (A-M systems WA, USA) on a horizontal micropipette flame puller (Flaming-Brown P-87, Sutter Instruments, Novato, CA). The microelectrodes were sealed in this silicate glass capillary for insulation.

The working microelectrodes were prepared by joining an electrochemically activated carbon fiber of 25 µm (WPI Carbon Wire) with a copper wire of approximately 0.2 mm diameter using silver epoxy. This assembly was then inserted into the flame-pulled glass micropipette tip of approximately the same diameter as the carbon fiber being used. Lastly, both ends were sealed using ethyl cyanoacrylate. All these preparation steps were performed under a light microscope. A sketch of the electrode is shown in
Figure 3.4. Properties such as high conductivity, non-toxicity, non-reactivity under various conditions, flexibility and small size have made carbon fibers the top choice in microelectrode preparation. However, the carbon fibers are quite fragile, and many electrodes were necessary for these measurements.

Single particles were buried within resin epoxy in a way that only one surface of it was exposed to the electrolyte. The exposed surface was polished. The flat surface area was calculated from digital photographs taken under microscope using Image J freeware (Image J). Every image taken was calibrated with a wire with known diameter placed next to the embedded particle. All data were normalized to the planar surface area of the electrode.
3.3.5.2 Micro Positioning System

The experimental setup is shown in Figure 3.5. The instrumental setup used during the course of the experiments consisted of a conventional stereo microscope (Meiji EMZ-13TR) equipped with a digital microscope eyepiece camera (Lumenera Infinity 1-3) connected to a PC through a USB interface. With this system, acquisition of both still pictures and real-time video images for further processing and undertaking measurements under optical control was possible. An XYZ motorized micromanipulator (Sutter Instruments MP-225) mounted on one side of the microscope allowed accurate positioning of the single pyrite particles in electrical contact with the microelectrode.

Figure 3.4  Working microelectrode assembly (with permission from Rivera-Vásquez, 2010).
The tip of the working electrode was put in contact with a single pyrite particle mounted in epoxy and immersed in electrolyte solution by handling the micromanipulator using a remote controller (see Figure 3.5). The microelectrode was positioned a certain distance above the surface and then lowered in very small increments. The measurement started when the microelectrode tip touched the particle. In this step, relative movements between the microelectrode and the particle must be avoided in order to maintain microelectrode-particle electrical contact. Every step of this process was controlled under the microscope. This method generally resulted in the deformation of the microelectrode tips, rendering them useless for further testing.

### 3.3.6 Electrochemical Cell for Micro Electrode Technique

A conventional three-electrode electrolytic cell was used for the electrochemical experiments. All electrochemical measurements were performed in a solution consisting of 0.5M sulfuric acid, 0.005M ferric sulfate and 0.005M ferrous sulfate. Dissolved air in the solution was purged by sparging with argon for 20 minutes before and during the experiment. All experiments were conducted at room temperature.

Pyrite particles in contact with the microelectrode were used as the working electrode (WE). A saturated calomel electrode (SCE) was used as the reference; all further potentials quoted in this study are vs. SCE (+244 mV vs. SHE at 25°C). The reference electrode was always isolated from the cell by a Luggin capillary containing the electrolyte. In order to limit chloride ion leakage from the saturated calomel reference electrode to the measurement system a salt-bridge reference electrode was used. The counter electrode (CE) was a platinum wire with a length of 5 cm and a diameter of 1 mm. Impedance spectroscopy was measured using the same potentiostat as mentioned in the previous section. A sinusoidal potential modulation with amplitude of ±5 mV was superimposed on the potential 420mV vs. SCE. The frequencies used for impedance measurements ranged from 100 kHz to 50 mHz. The program ZSimpWin 3.10 from EChem Software was used to fit the experimental data to the most suitable equivalent electrical circuit.
For all of the Mott-Schottky measurements, the voltage change was controlled potentiostatically. The capacitance under different DC biasing and for different frequencies (10 kHz and 20 kHz) was measured by the same potentiostat. No frequency dependence of capacitance was observed in the present case.

To measure solution potential of the redox couple, a solution redox potential probe (Analytical Sensors) was used. The probe was attached to the aforementioned multi-channel digital controller to read the data.

![Figure 3.5 Schematic representation of the experimental electrochemical cell. a) Cell b) pyrite single particles c) micromanipulator and controller d) working electrode e) reference electrode f) glass frit g) gas sparger h) electrolyte solution (with permission from Rivera-Vásquez, 2010).](image-url)
3.4 Raman Spectroscopy

Micro Raman spectroscopy offers a wealth of fine chemical and molecular information about the sample surfaces at a micrometric spatial resolution. Micro Raman spectroscopy provides a powerful tool for non-destructive, real time characterization of solid and aqueous samples, which enables researchers to examine various mineral surfaces such as electrochemically oxidized pyrite surfaces. Hence, micro Raman spectroscopy is a means for precise analysis of reacted pyrite surfaces, providing additional insight into the oxidation pathways of sulfide minerals (Pisapia et al., 2010).

X-Ray photoelectron spectroscopy has been extensively utilized to analyze and investigate the surface products of pyrite oxidation (Descostes et al., 2000; Knipe et al., 1995; Murphy and Strongin, 2009; Mycroft et al., 1990; Nesbitt and Muir, 1994; Scaini et al., 1997; Toniazzo et al., 1999). However, studies applying this technique suffer from the fact that the alteration of the surface due to the vacuum conditions and special sample handling requirements can cause some additional uncertainty in the interpretation of results.

3.4.1 Background

Raman spectroscopy, a vibrational technique, was first observed experimentally in 1928, and was named in honor of its discoverer, C.V. Raman, who, along with K.S. Krishnan published the first paper on this technique (Karst, 1999). Due to the weakness of the Raman scattering (one in every $10^6$–$10^8$ photons which scatter is Raman scattered), it was the introduction of laser that revived Raman spectroscopy as a useful analytical technique in the 1960s (Smith and Dent, 2005).

In vibrational spectroscopy, the energy changes that cause nuclear motion are used. If only electron cloud distortion occurs in scattering, the scattering process is regarded as elastic scattering in which the scattered radiation is the same frequency as the incident radiation ($\nu_0$). This is called Rayleigh scattering. On the other hand, inelastic scattering means that the frequency of photons of the laser changes upon interaction with a sample. When nuclear motion is involved in the scattering process energy will be
transferred resulting in a difference in the energy of the scattered photon from that of the incident photon by one vibrational unit. This is Raman scattering (Smith and Dent, 2005). Figure 3.6 depicts the energetics of the Raman process. The $\nu_0 - \nu_m$ and $\nu_0 + \nu_m$ lines are called the Stokes and anti-Stokes lines, respectively.

Infrared (IR) and Raman spectroscopy both measure the vibrational energies of molecules but IR spectroscopy is absorption spectroscopy and Raman spectroscopy is scattering spectroscopy. For a vibrational motion to be IR active, there must be a change in either the dipole moment of the molecule or charge distribution associated with it. For a vibration to be Raman active, there must be a change in polarizability of the molecule. If the vibration does not alter the polarizability of the molecule, the dipole oscillates only at the frequency of the incident radiation. Polarizability is a measure of the capability of inducing a dipole moment in response to an applied electric field. (Nair, 2006).
Figure 3.6  Diagram of the Raman and Rayleigh scattering of excitation at a frequency $\nu_0$.  The laser excitation frequency ($\nu_0$) is represented by the upward arrows and is much higher in energy than the molecular vibrations.  The frequency of the scattered photon (downward arrows) is unchanged in Rayleigh scattering but is of either lower or higher frequency in Raman scattering (adapted from Larkin, 2011).

3.4.2 Raman Techniques

3.4.2.1 Normal Raman spectroscopy

Normal Raman spectroscopy is used as a non-destructive technique to provide characteristic fundamental vibrations that are employed for the elucidation of molecular
structure of different classes of materials. Some features of Raman spectroscopy are as follows:

- Beam diameters do not exceed 1–2 mm, and the appropriate use of microscope objective lenses can even limit the beam to <2 μm diameter. This means that a small sample volume will suffice. More modern Raman instruments are equipped with mapping programs which enables researcher to make detailed investigations of lateral surface variations.
- Samples used for study can be in the form of solids, liquids and gases.
- Selection rules for an IR or Raman active mode of vibration are different. Some vibrations are only Raman-active while others are only IR-active. For a mode of vibration to be IR active, it must give rise to a change in the molecular electric dipole moment. For a mode of vibration to be Raman active, it must give rise to a change in the polarizability of the molecule. The molecular symmetry also determines the selection rules for occurrence of IR or Raman active vibrations.
- Water shows a weak Raman spectrum. Generally, Raman spectra of samples in aqueous solutions can be obtained without major interference from water vibrations.
- It requires little or no special sample preparation for analysis.
- Raman data can be used to complement IR data. Generally, stretching vibrations of covalent bonds generate stronger Raman vibration than those of ionic bonds.
- Reliable information about the symmetry of a normal vibration in solution where molecules are randomly oriented can be obtained by measuring depolarization ratios. IR spectra are not useful for this application.
- With one single recording the region from 4000 to 50cm\(^{-1}\) can be covered in Raman spectroscopy without any need to change gratings, beam splitters and detectors.
- Vibrational (Raman and IR) Spectroscopy is unique in that it can be applied to the solid state as well as the liquid and gaseous state. Other techniques such as X-Ray diffraction can only be used for crystalline materials.
Disadvantages of Raman spectroscopy include:

- A powerful laser source is required to observe the weak Raman scattering effect. This laser can cause overheating and/or photodecomposition of the sample if proper care is not taken.
- Some molecules exhibit fluorescence when irradiated by the laser beam. Fourier Transform (FT)-Raman instruments are used to overcome fluorescence interference.
- High-resolving power is difficult to obtain in the UV-Visible region of Raman spectroscopy. Thus, it is more difficult to acquire rotational and rotation-vibration spectra with high-resolution in Raman than with IR spectroscopy (Nakamoto, 1994).

### 3.4.2.2 Surface Enhanced Raman Spectroscopy (SERS)

A great disadvantage of Raman spectroscopy results from the very small cross section of the Raman process (Kneipp et al., 2002). The discovery of Fleischmann et al. (1974) that Raman signals from pyridine adsorbed at roughened silver electrodes were enhanced, unleashed a torrent of investigations that has hardly abated (Kerker, 1984). SERS is about amplifying Raman signals (almost exclusively coming from molecules) by several orders of magnitude. The amplification of the signals originates from the electromagnetic interaction of light with metals. This interaction produces large amplifications of the laser fields through excitations known as plasmon resonances.

In this technique the molecules must be adsorbed on the metal surface, or be very close to it (less than 10 nm). In order for the metals to have an enhancing effect, they need to be in the form of metallic nano-structures. This encompasses a range of different SERS substrates, from metallic colloids in solution to substrates fabricated by nano-lithography or self-organization (Le Ru 2009).

The exact reason for such dramatic enhancement is still the subject of considerable controversy. The intensity of Raman scattering is proportional to the square of the induced electric dipole moment. There has been general agreement that the SERS
effect results from either enhancement of the electrical field or enhancement of polarizability. Enhancement of the electric field, also known as the electromagnetic effect, is considered to come mainly from a geometrically defined surface plasmon resonance at metal nanoparticles such that the electromagnetic field at the surface is enhanced over that of the bulk due to surface plasmon resonances. Enhancement of polarizability, also known as the chemical effect, comes from chemisorption interaction. This originates from a complex mechanism which is associated with the excited state of the molecule/metal system and with the charge transfer between the molecule and the metal surface known as photon-driven charge-transfer enhancement. For the noble-metal systems, the electromagnetic effect enhancement generated from metal nanostructures plays a dominant role (Tian et al., 2002).

When the correct wavelength of radiation strikes a rough metallic surface, the plasma of conduction electrons will oscillate collectively. This oscillation is unable to propagate into the bulk and produces a localized surface plasmon which, if in resonance with the incident radiation, creates a large electromagnetic field around the particle or roughness feature (Kerker, 1984).

There are some obstacles in using the SERS as a powerful surface technique:

- Only gold, silver, and copper can provide large enhancement of Raman spectra. However, Tian et al. (2002) have developed procedures to generate SERS on transition metal substrates via roughening and confocal Raman microscopy.
- Even for these metals, surface morphology with a roughness scale of 50~200 nm is vital to exhibit a large enhancement.
- Although a number of SERS mechanisms have been proposed to explain its experimental characteristics, no mechanism can explain all of the observed effects (Tian et al., 2002).

### 3.4.3 Raman Investigation in the Present Study

Raman Spectra were acquired from Raman scattering under excitation with the 514.5 nm (green) line of an argon ion laser (Reliant, laser physics). A Renishaw instrument
equipped with a CCD detector and an inVia Raman microscope oriented normal to the sample were used. The microscope was equipped with a ×50 objective lens (numerical aperture of 0.75) to focus the laser. During Raman spectroscopy, laser power was kept below 0.5 mW at the sample surface to avoid any possible laser-induced sample alteration. Each spectrum was acquired utilizing 10% of the maximum laser power and summing 20 scans involving 50 s of laser exposure, providing an adequate signal-to-noise ratio. Sample preparation simply required placing mineral particles on a glass slide using tweezers. The instrument was calibrated against the Raman signal of Si at 520 cm$^{-1}$ employing a standardized silicon wafer (111), before the micro Raman measurements.

Raman spectrometry begins with viewing an optical image acquired by a built-in video camera and the microscope objective lens of the sample on the attached computer monitor. This optical image is useful to help guide movement of the motorized XYZ stage in order to obtain point-by-point analysis of the desired microscopically small samples. By selecting the appropriate microscope objective lens, adjusting the working distance between sample and the objective lens and adjusting the laser power intensity, the laser is focused on the micro-scale area of the work material (Teo, 2007).

3.4.4 UV-Vis Spectroscopy in the Present Study

The UV-Visible spectra were measured with a Shimadzu UV-Vis 2401PC spectrophotometer in the range 200–1000 nm using a 1-cm optical path-length quartz cuvette.

3.5 Synthesis of Gold and Silver Nanoparticles

Colloidal gold was synthesized using the following procedure; 0.85 g of solid HAuCl$_4$ was dissolved in 25 mL of water to prepare a 0.1 M HAuCl$_4$ solution, 1 mL of which was added to 32 mL of water to produce a 3 mM solution. Subsequently, a predetermined volume of 0.1 M Na$_2$S solution, required to obtain a Na$_2$S:HAuCl$_4$ molar ratio of 0.7 (Mikhlin et al.), was added after which the solution turned red. In order to prepare the colloidal silver, a silver nitrate salt (AgNO$_3$) was used as a starting material and sodium
tetrahydridoborate (NaBH₄) as a reducing agent. In this step, 10 mL of 1.0 mM AgNO₃ solution was added to 30 mL of 2.0 mM NaBH₄ solution (Solomon et al., 2007). The solution turned light yellow after the addition of silver nitrate. All solutions were continuously stirred using a magnetic stirrer plate. In order to inhibit aggregation, reaction conditions including stirring time and relative reagent concentrations were controlled.

It has been previously shown that, in the presence of pyrite, Au and Ag NPs reduce and spontaneously deposit on the mineral surfaces (Mikhlin et al., 2009 and 2011). Thus, shortly after preparation of the sols, ground pyrite was added and Au and Ag NPs were deposited on the surface at 20±1°C. The reacted samples were rinsed with water before transfer to an electrochemical cell.
CHAPTER 4: Electrochemical Study of Leached Chalcopyrite

4.1 Atmospheric Leaching of Chalcopyrite with Pyrite

The following variables were set in the leaching tests of chalcopyrite concentrate: initial acid content 0.5 M sulfuric acid, solution potential 420 mV vs. SCE, temperature 80°C. One test was conducted to observe the rate of copper extraction in ferric sulfate solution in the absence of added pyrite. In four other tests, four different pyrite samples were added to chalcopyrite with a pyrite-to-chalcopyrite mass ratio (Py:Cp) of 3:1. The results of these experiments are shown in Figure 4.1.

As reported by Dixon et al. (2008), pyrite addition has a significant effect on the kinetics of copper extraction. The test without added pyrite achieved less than 40% copper extraction after 50 hours. The addition of pyrite dramatically increased the extraction of copper. As shown in Figure 4.1 the rate of copper extraction with pyrite #1 reached 90% after 10 hours. Pyrites #2, #3 and #4 proved to be less effective catalysts for copper extraction. This may be because of possible differences in electrochemical and semiconducting properties of the pyrites coming from different sources and their probable influence on the passive film formed during leaching around the chalcopyrite. This is evident from the similar kinetic behavior of chalcopyrite leaching in all three tests during the first few hours of leaching. Small concentrations of common impurities, particularly silver, which is a well-known catalyst, can tremendously impact the electrical and electrochemical properties of pyrite. This potentially rich area of study is under further investigation in our research group, and a major enhancing effect of silver adsorbed on pyrite catalysts in the Galvanox™ process has been reported (Nazari et al., 2011). Munoz et al. (1979) also measured the electrical conductivity of the elemental sulfur reaction product encapsulating chalcopyrite to be 7.6 times the conductivity of pure crystalline orthorhombic sulfur, this is caused by existing impurities in the elemental sulfur reaction product. Munoz et al. (1979) considered the role of minor impurity elements in increasing the electrical conductivity of pure sulfur by up to
two orders of magnitude as a well known fact. Moreover, the distribution and combination of electrically active elements which exist in pyrite as impurities such as As, Co and Ni have been reported to influence the mechanisms of reactions occurring at pyrite surfaces (Savage et al., 2008).

Figure 4.1 Copper extraction from chalcopyrite leaching experiments in ferric sulfate solution.

Scanning electron microscopy and energy dispersive X-ray analysis were used to investigate further the different layers formed on the surface of chalcopyrite. Figure 4.2 a shows an electron micrograph of a chalcopyrite sample leached for 45 hours in the absence of pyrite. Figure 4.2 b shows a chalcopyrite sample leached for 45 hours in the presence of pyrite #4 and Figure 4.2 c shows a chalcopyrite sample leached for 10 hours in the presence of pyrite#1. In those cases where the copper extraction is slow and incomplete, as shown in Figure 4.2 a and b, the elemental sulfur layer formed
around the chalcopyrite particles has a different structure compared to when the copper extraction is rapid, as shown in Figure 4.2 c. Also the different sulfur morphologies shown in Figure 4.2 b and c reveal that different pyrite samples can have a remarkably different influence on chalcopyrite leaching. Pyrite, in addition to its galvanic effect over chalcopyrite, induces elemental sulfur to form differently. The highly porous sulfur morphology shown in Figure 4.2 c is a sign of rapid and successful leaching. More research needs to be done in this area to determine the effect of pyrite on sulfur morphology during leaching.

An observation which suggests itself in comparing Table 3.2 and Figure 4.1 is a strong correlation between effectiveness of the pyrite on the kinetics of the chalcopyrite leaching with the amount of silver in the pyrite samples.
Figure 4.2  SEM micrograph and EDX analysis of the chalcopyrite sample leached (a) in the absence of pyrite after 45 h, (b) in the presence of pyrite concentrate #4 after 45 h, and (c) in the presence of pyrite concentrate #1 after 10 hours.
4.2 Cyclic Voltammetry (CV) of Chalcopyrite and Pyrite

First, making a reliable CPEE for quantitative electrochemical measurements was attempted. In order to optimize the behavior of the paste electrodes and the reproducibility of the results, various parameters were considered during the construction process. These parameters included: choice of carbon powder and pasting liquid, carbon-to-liquid ratio, and mode of preparation and homogenization of the carbon paste. In a similar vein, parameters of the cyclic voltammetry scans were also considered, including: scan rate, equilibration time, scan direction and number of cycles.

The reproducibility of the analytical response was assessed by comparing peak heights of 10 replicate cyclic voltammetry scans under various conditions (Figure 4.3). The relative standard deviation (RSD) values obtained for the CPEE for the highest anodic peak were in the range of 50% to 90%, which indicates rather poor reproducibility for this type of electrode in comparison to 8% for SPCPE electrode shown in Figure 4.4.

One possible factor that was considered to have an effect on reproducibility was the time during which an electrode is in contact with an electrolyte. The longer the time, the higher the recorded current will be during cyclic voltammetry. To investigate this assumption, a set of experiments were conducted in which each electrode was used only once, rather than the more conventional approach of using the same electrode by renewing the surface with a spatula. No noticeable improvement was observed in the RSD values.
Figure 4.3  Comparison of anodic peak heights of 10 different chalcopyrite electrodes using CPEE technique.
Figure 4.4  Comparison of anodic peak heights of 10 different chalcopyrite electrodes using SPCPE technique.

Another potential factor contributing to reproducibility of results is a variation in the number of electroactive particles at the surface from one test to another. In order to investigate this effect, scanning electron microscope (SEM) images were taken of the surface of the electrodes, as shown in Figure 4.5. The proportion of the total surface area occupied by electroactive mineral particles was estimated using Image J software (Image J), and was found to vary from 20 to 70%. This difference in surface coverage by electroactive mineral particles is obvious when comparing Figure 4.5 a and b. This is the probable cause of the very different results obtained in the electrochemical experiments since the recorded current relies predominantly on the exposed surface area of the electroactive particles.
Figure 4.5  SEM micrographs of two CPEE electrodes showing different surface coverage by electroactive particles.

In addition, a technical problem occurred during electron microscopy; the vacuum in the SEM chamber forced carbon paste out of the syringe. This rendered it impossible to measure the exposed surface area of electroactive mineral particles, and to normalize the cyclic voltammetry data on that basis.

It was concluded that success with CPEE relies on experimental skill to a great extent. This disadvantage of CPEE significantly limits their applicability in practical quantitative analysis. Each carbon paste represents an individual case with unique physico-chemical and electrochemical properties. The choice of carbon paste components, their quality and ratio in the mixture, as well as the method of preparation of carbon pastes, their optimal homogenization and the duration of contact with electrolyte can all impact the resulting behavior of a CPEE. Although the parameters were fixed in this research and known procedures were chosen for testing measurements, there were still many unknown aspects of the CPEE which made it impossible to arrive at a definitive
conclusion or to make accurate comparisons of the cyclic voltammetry behavior of different electrodes.

On the other hand, with a relative standard deviation of less than 8% (Figure 4.4), solid paraffin-based carbon paste electrodes (SPCPE) appear to be a promising method for further investigation of the electrochemistry of mineral powders.

An SEM micrograph (Figure 4.6) taken after a chalcopyrite SPCPE was washed with water shows that the particles were well immobilized on the electrode surface, and that roughly 95% of the surface is covered by electroactive mineral particles.

![SEM micrograph of SPCPE electrode surface after rinsing with water.](image)

In order to study the electrochemical responses of partially leached pyrite and chalcopyrite surfaces, cyclic voltammetry was conducted in combination with batch leaching tests. Cyclic voltammetry involves oxidation of the electrode surface during a linear potential scan and analyzing the products of anodic oxidation from the characteristics of their reduction on a subsequent reverse potential scan. In order to understand the voltammetric behavior, knowledge of possible reactions which can occur
between the various mineral species and dissolved ions is required (Hamilton and Woods, 1981).

The stability of solid paraffin-based carbon electrodes with no electroactive mineral added was tested in solution over the working potential range. The resulting voltammogram showed very small values of current density compared to electrodes with electroactive particles. This indicates that the solid paraffin-based carbon electrode is inert and stable over the potential range studied, and that the background current generated by this electrode is negligible.

4.2.1 Electrochemical Behavior of Chalcopyrite

First, voltammograms of freshly ground chalcopyrite and pyrite using SPCPE were plotted in order to compare the data obtained with those found in the literature using other types of electrodes.

The electrochemical behavior of chalcopyrite and pyrite has been well documented by a number of researchers, although minor differences between the various investigations exist.

Voltammograms for chalcopyrite, in 0.5 M sulfuric acid at pH 0.3, are shown in Figure 4.7. The potentials used in this study were maintained less than 800 mV vs. SCE, where the main chalcopyrite decomposition reaction occurs. Comparison of a voltammogram for a polished macro chalcopyrite electrode with a voltammogram obtained using the SPCPE shows good agreement between them (Figure 4.8). It is worth noting that the anodic and cathodic peaks showed different current density values. This is because the surface area of a particulate electrode cannot be measured accurately, due to the roughness of the surface, compared to a macro electrode.

In the voltammograms shown in Figure 4.7, the solid line represents a scan in the anodic direction, and the dashed line represents a scan in the cathodic direction. These measurements were initiated at the open circuit potential (OCP). The electrode potential was allowed to stabilize for 10 min before starting the measurements. In order
to ensure reproducibility, tests were begun only after the drift rate in OCP fell below 1 mV/min. Experimental conditions during the electrochemical measurements were set as follows: temperature 20°C, scan rate 20 mV/s, and solution composition 0.5 M H₂SO₄ without agitation unless otherwise noted.

![Cyclic voltammogram showing oxidation and reduction of chalcopyrite using a SPCPE electrode in 0.5 M H₂SO₄ solution (solid line = positive sweep, dashed line = negative sweep).](image)

Figure 4.7  Cyclic voltammogram showing oxidation and reduction of chalcopyrite using a SPCPE electrode in 0.5 M H₂SO₄ solution (solid line = positive sweep, dashed line = negative sweep).

One anodic current peak, A1, is observed in scanning from OCP to 800 mV vs. SCE before the main active decomposition current peak. Previous research conducted by Price and Warren, (1986) revealed that this peak, which they referred to as the ‘prewave’, corresponds to the partial oxidation of chalcopyrite to iron- and copper-deficient compounds as shown in reaction (R4.1), where \( y > x \).
\[
\text{CuFeS}_2 = Cu_1-xFe_{1-y}S_{2-z} + x Cu^{2+} + y Fe^{2+} + z S^0 + 2(x + y) e^- \tag{R4.1}
\]

Figure 4.8 Cyclic voltammograms of chalcopyrite electrodes showing a good agreement between two types of electrodes in 0.5M H\textsubscript{2}SO\textsubscript{4} solution (solid line=macro polished electrode, dashed line= SPCPE).

The prewave represents the initial stage of the dissolution of chalcopyrite and determines the surface properties of the mineral during the rest of the dissolution process. Biegler and Horne, (1985) and Biegler and Swift (1979b) interpreted the prewave region as a surface oxidation process involving a thin layer of chalcopyrite.

Lazaro and Nicol (2006) have shown some evidence for the formation of Cu\textsuperscript{2+}, Fe\textsuperscript{2+}, and soluble sulfur species during the initial stages of chalcopyrite dissolution at 60°C. Holliday and Richmond (1990) show a sequential mechanism for the surface oxidation which consists of an initial rate-determining step for the production of adsorbed Cu\textsuperscript{2+}.
followed by the production of Fe$^{2+}$. These reactions are responsible for making a passive surface layer on the mineral and hindering the dissolution rate. Parker et al. (1981b) referred to the product causing the prewave peak as a polysulfide, which has semiconducting properties. Yin et al. (1995), using XPS data obtained from two different samples, one a cleaved fresh surface and the other an electrochemically oxidized sample, concluded that iron was oxidized and dissolved from the surface of chalcopyrite, leaving behind a metastable phase at the surface with the formula CuS$_2$ (villamaninite) as the passive layer.

A recent study has shown that the peak attributed as A1 in Figure 4.7 actually involves two passive layers growing on top of each other within that potential range (Ghahremaninezhad et al., 2010). The study showed that the passive layer has the composition Cu$_{1-x}$Fe$_{1-y}$S$_2$ ($y >> x$) at potentials near the open circuit potential (OCP) of chalcopyrite (OCP to 500 mV vs. SCE) and in the higher potential range, a second passive layer (Cu$_{1-x-z}$S$_2$) forms according to reaction (R4.2).

$$\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_2 = \text{Cu}_{1-x-z}\text{S}_2 + z\text{Cu}^{2+} + (1-y)\text{Fe}^{2+} + 2(1-y+z)\text{e}^- \quad (R4.2)$$

As shown in Figure 4.9 when the final grinding of the concentrate and electrode preparation is carried out in an oxygen-free (argon) environment, and the final electrodes are exposed to air for less than one minute during transport to the experimental apparatus, the prewave peak is more prominent compared to when the grinding and electrode preparation are deliberately exposed to air. Comparison of the two plots shows that the prewave bears a direct relationship to the degree of chalcopyrite pre-oxidation. When the surface of chalcopyrite is not significantly pre-oxidized, a higher peak current is recorded. However, exposure to air causes a passive layer film to form, which decreases the extent of subsequent electrochemical oxidation in the prewave region. Yin et al. (1995) observed a similar phenomenon in hydrochloric acid media.

In the reverse scan, the reduction of surface products formed in the prewave region occurs at peaks C1 and C2. This idea is supported by the dashed-line voltammogram in Figure 4.7 which shows the absence of these peaks when the initial scan is started in
the cathodic direction. In Figure 4.7, peak C2 has a much higher intensity than C1 and has overshadowed peak C1. As can be seen in Figure 4.10, these peaks show a higher intensity in subsequent scans after anodic scans have produced more surface products of chalcopyrite oxidation. These observations are consistent with the results of other researchers (Lazaro et al., 1995; Lu et al., 2000; Price and Warren, 1986).

![Graph showing cyclic voltammogram](image)

**Figure 4.9** The effect of atmospheric electrode oxidation on the cyclic voltammogram of chalcopyrite using a SPCPE electrode in 0.5M H₂SO₄ solution (solid line = electrode prepared in oxygen-free medium; dashed line = electrode exposed to air).

Holliday and Richmond (1990), who observed three cathodic peaks in total; attributed peaks C1 and C2 to reactions below:

\[ \text{Fe}^{3+} + e^- = \text{Fe}^{2+} \]  

(R4.3)
\[
\begin{align*}
\text{Cu}^{2+} + S^0 + 2 e^- &= \text{CuS} \quad \text{(R4.4)} \\
\text{Cu}^{2+} + 2 e^- &= \text{Cu}^0 \quad \text{(R4.5)}
\end{align*}
\]

According to them, elemental sulfur and dissolved species such as \( \text{Cu}^{2+} \) and \( \text{Fe}^{3+} \) are the expected candidates for reduction on the surface of the electrode. They did not observe these peaks using rotating disc electrodes (RDE), since any ions produced were removed from the vicinity of the rotating electrode.

![Cyclic voltammograms showing continuous cycling of the potential between 0.8 and −0.5 V for a chalcopyrite electrode using a SPCPE electrode in 0.5M H\(_2\)SO\(_4\) solution.](image)

**Figure 4.10** Cyclic voltammograms showing continuous cycling of the potential between 0.8 and −0.5 V for a chalcopyrite electrode using a SPCPE electrode in 0.5M H\(_2\)SO\(_4\) solution.

In Figure 4.7, at potentials between −200 mV and −500 mV, one peak can be seen, but there are actually two peaks in that potential region: one at −250 mV (C3) and the other at about −400 mV (C4). Peak C3 at −250 mV is overshadowed by peak C4, which has
a higher magnitude. According to Biegler and Swift (1976), peak C3 can be attributed to the reduction of the remnant chalcopyrite to an intermediate copper sulfide phase such as talnakhite (Cu$_9$Fe$_8$S$_{16}$), mooihoekite (Cu$_9$Fe$_9$S$_{16}$) or bornite (Cu$_5$FeS$_4$). Talnakhite and bornite, for example, can form according to reactions below:

\[
9 \text{CuFeS}_2 + 4 \text{H}^+ + 2 \text{e}^- = \text{Cu}_9\text{Fe}_8\text{S}_{16} + 2 \text{H}_2\text{S} + \text{Fe}^{2+} \quad (\text{R}4.6)
\]

\[
5 \text{CuFeS}_2 + 12 \text{H}^+ + 4 \text{e}^- = \text{Cu}_5\text{SFeS}_4 + 6 \text{H}_2\text{S} + 4 \text{Fe}^{2+} \quad (\text{R}4.7)
\]

At potentials more negative than peak C3, in solutions at pH near zero, by referring to the Pourbaix diagram of copper sulfides it is predicted that the copper-containing solid phases found at equilibrium are, in order of decreasing potential: chalcopyrite, bornite, chalcocite (Cu$_2$S) and elemental copper. Hydrogen evolution also occurs at these lower potentials. When chalcocite is formed, iron is completely removed from the chalcopyrite lattice, as per reaction (R4.8):

\[
6 \text{CuFeS}_2 + 6 \text{H}^+ + 2 \text{e}^- = \text{Cu}_2\text{S} + 3 \text{H}_2\text{S} + 2 \text{Fe}^{2+} \quad (\text{R}4.8)
\]

As the potential sweep is reversed in direction at −500 mV, the current swings positive at about 60 mV. Three anodic peaks A2, A3 and A4 can be observed in this part of the scan. These peaks are attributed to the oxidation of products produced during the cathodic sweep. \(\text{H}_2\text{S}\), produced during the formation of chalcocite as per reaction (R4.8), is oxidized as per reaction (R4.9) and results in anodic peak A2.

\[
\text{H}_2\text{S} = \text{S} + 2 \text{H}^+ + 2 \text{e}^- \quad (\text{R}4.9)
\]

Furthermore, any copper metal formed during the cathodic sweep is oxidized to cupric in this potential region. It is worth noting that the presence and prominence of these peaks relies extensively on the lower limit of the cathodic potential scan and the intensity of agitation. Peaks A3 and A4 correspond to the oxidation of chalcocite to a series of non-stoichiometric sulfides \(\text{Cu}_{2-x}\text{S}\) as per reaction (R4.10).

\[
\text{Cu}_2\text{S} = \text{Cu}_{2-x}\text{S} + x \text{Cu}^{2+} + 2x \text{e}^- \quad (\text{R}4.10)
\]

If the charge associated with peak A4 equals the charge associated with peaks C1 and C2, then it is expected that \(x\) will have a value close to 1, which means that covellite (Cu$_2$S) would be the main reaction product (Lu et al., 2000; Price and Warren, 1986).
4.2.2 Electrochemical Behavior of Pyrite

The voltammogram of pyrite #4 in 0.5 M sulfuric acid obtained by an anodic potential scan from the OCP is shown in Figure 4.11. When the scan is initiated in the anodic direction, three anodic current peaks A1, A2 and A3 are observed. During the cathodic scan, two cathodic peaks C1 and C2 are produced.

During the initial anodic scan, the current was very low until the potential reached 600 mV vs. SCE, after which there was a sharp rise in current (peak A1 in Figure 4.11). During oxidation of pyrite, iron deficient pyrite, sulfate and polysulfides form. Small, time-dependent currents observed at potentials below 600 mV on the first scan suggest that such a surface layer inhibits oxidation. Doyle and Mirza (1996) proposed another theory; a p-type semiconducting layer formed on the surface generates a p-n junction with underlying pyrite that is reverse biased for passing an anodic current. They did not present any experimental evidence to support this claim. This idea is in contrast with Biegler and Swift (1979a) who found no systematic influence of semiconductor type on the kinetics of anodic dissolution of pyrite.

Above 600 mV, the initial surface layer undergoes extensive oxidation as follows:

\[
Fe_{1-x}S_2 + 8 H_2O = (1 - x) Fe^{3+} + 2 HSO_4^- + 14 H^+ + 3(5 - x) e^- \quad (R4.11)
\]

Above 800 mV, the current-voltage relationship is approximately linear, indicating that the current is completely ohmic in nature. These results are essentially in agreement with other researchers' results (Biegler and Swift, 1979a; Doyle and Mirza, 1996). No gas evolution was observed in the potential range of peak A1.

A cathodic peak C1 was observed at about 400 mV. This peak is attributed to ferric reduction according to reaction (R4.3). In order to confirm this, cyclic voltammetry tests were performed in electrolytes with different ferric concentrations. With increasing concentrations of ferric from 0 to 0.05 M in the electrolyte, the size of this peak was amplified progressively, thus proving that this peak is caused by the reduction of ferric formed during previous anodic scans. The results shown in Figure 4.12 agree with the findings of Doyle and Mirza (1996).
Figure 4.11  Cyclic voltammogram showing the oxidation and reduction of pyrite #4 using a SPCPE electrode in 0.5M H₂SO₄ solution.

The cathodic current began to increase significantly below about −240 mV (peak C2 in Figure 4.11). At this potential and at pH near zero, pyrite decomposes to H₂S and Fe²⁺, as per reaction (R4.12).

\[
\text{FeS}_2 + 4 \text{H}^+ + 2 e^- = \text{Fe}^{2+} + 2 \text{H}_2\text{S}
\]  \hspace{1cm} (R4.12)
Figure 4.12  Cyclic voltammogram focusing on peak C1, showing the reduction of ferric ions on pyrite as a function of applied potential at various concentrations of ferric ions using a SPCPE electrode in 0.5M H$_2$SO$_4$ solution.

Alternatively, according to Hamilton and Woods (1981), this peak can be assigned to the reduction of electrochemically formed sulfur as per reaction (R4.13).

\[
S + 2H^+ + 2e^- = H_2S \tag{R4.13}
\]

H$_2$S evolution is the major reaction occurring during the first cycle. When the scan direction was reversed to the anodic direction on the first cycle, relatively high cathodic current continued to be passed until the potential reached about $-70$ mV, beyond which anodic current started to pass. There is a trivial peak A3 corresponding to the reversal of reactions (R4.12) and (R4.13). The size of this peak is expected to be very small since H$_2$S is dispersed and Fe$^{2+}$ is soluble.
As the potential increases, the anodic currents are caused by the formation of iron-deficient pyrite and Fe$^{2+}$, as per reaction (R4.14).

$$\text{FeS}_2 = \text{Fe}_{1-x}\text{S}_2 + x \text{Fe}^{2+} + 2x e^-$$  \hspace{1cm} (R4.14)

Peak A2 at about 500 mV represents oxidation of Fe$^{2+}$ to Fe$^{3+}$, as per reaction (R4.15).

$$\text{Fe}^{2+} = \text{Fe}^{3+} + e^-$$  \hspace{1cm} (R4.15)

The mild anodic current between peaks A2 and A1 corresponds to the formation of iron-deficient pyrite and Fe$^{3+}$, as per reaction (R4.16).

$$\text{FeS}_2 = \text{Fe}_{1-x}\text{S}_2 + x \text{Fe}^{3+} + 3x e^-$$  \hspace{1cm} (R4.16)

Above 600 mV, high anodic currents are measured (peak A1 in Figure 4.11) which can be attributed to the dissolution of the iron deficient sulfide generated by reaction (R4.14). In the second and succeeding cycles, formation of more iron-deficient pyrite on the surface causes considerably higher anodic currents than those measured in the first cycle within the potential window of 600 and 450 mV (Doyle and Mirza, 1996).

The charge passed during anodic and cathodic processes can be determined by integration of the current with respect to potential in order to quantify the oxidation product formed. The difference between charge passed by anodic and cathodic reactions is the result of soluble species forming during oxidation, which diffuse into solution and become unavailable for subsequent reduction.

By comparing the voltammograms of Figure 4.7, Figure 4.11 and Figure 4.12, it can be seen that the peak potential of ferric reduction at the pyrite electrode is about 250 to 300 mV more positive than that recorded at the chalcopyrite electrode. This implies that ferric reduction occurs at a significantly lower overvoltage on pyrite than on chalcopyrite, which indicates that pyrite is significantly more electrocatalytic than chalcopyrite. This variable catalytic response is generally associated with differences in the strength of the adsorptive bonds between ferric ions and lattice atoms at the two mineral surfaces. The phenomenon is referred to as the “electronic factor” and depends on the nature of the rate-determining step. Geometric factors such as lattice spacing and lattice defects (edges, kinks, etc.) also affect bond strength and, hence, electrocatalysis. As explained
by Bockris et al. (2001), redox reactions such as ferric reduction on electrode surfaces involve intermediates adsorbed onto the electrode and therefore exhibit a rate that is substrate dependent.

Dixon et al. (2008) have suggested that, in contrast to what most investigators believe; it is the cathodic half-cell reaction (i.e., ferric reduction) which limits the overall rate of leaching, and not the anodic half-cell reaction (i.e., the mineral breakdown reaction). Hence the presence of pyrite in electrical contact with chalcopyrite as an alternative, electrocatalytic surface with a higher capacity for ferric reduction can alleviate the passive behavior of chalcopyrite in a ferric sulfate solution.

4.2.3 Electrochemical Behavior of Chalcopyrite Leached Alone

Figure 4.13 to Figure 4.16 depict voltammograms of chalcopyrite electrodes prepared from samples exposed to leaching for different periods of time ranging from 4.5 hours to 45 hours.

Measurements on the sample leached for 4.5 hours (Figure 4.13) show that, for the initial anodic scan, peak A1 is less prominent than it was in the initial anodic scan of fresh chalcopyrite (Figure 4.7). This suggests that less passive product film is formed on the electrode surface during the voltammetric scan, since this layer was already partly formed during leaching. For the cathodic scans, peaks C1 to C4 are better defined, which means that the magnitude of peaks C2 and C4 has decreased compared to the fresh sample thus allowing peaks C1 and C3 to be more easily distinguished. Upon reversing the scan toward the anodic direction at −500 mV, it is observed that peaks A2, A3 and A4 are more clearly pronounced. However, they occur at lower potentials than with fresh chalcopyrite. The current densities of most peaks are decreased by about 50 to 60% compared to the values recorded on fresh chalcopyrite. However, the value of the current density at 800 mV is similar to the value recorded for the fresh sample.
Figure 4.13  Cyclic voltammetry of copper concentrate after being leached in the absence of pyrite for 4.5 hours using a SPCPE electrode in 0.5M $\text{H}_2\text{SO}_4$ solution.

Voltammetry of the sample leached for 9 hours (Figure 4.14) shows that the prewave disappeared completely and a current density value of 0.1 mA/cm$^2$ was attained at 800 mV. All other peaks are still visible, although their values have decreased by roughly one order of magnitude compared to the 4.5 hour sample.

After 21.5 hours of leaching (Figure 4.15), peaks C2 and C4 are less pronounced than in all previous samples. This influence on peak C2 is due to less copper dissolving into the solution from the passive sample, which leaves fewer copper ions to be reduced during the cathodic scan. Similarly, the decrease in peak C4 implies less chalcopyrite reduction to chalcocite from a passive electrode surface.
Figure 4.14 Cyclic voltammetry of copper concentrate after being leached in the absence of pyrite for 9 hours using a SPCPE electrode in 0.5M H₂SO₄ solution.
Figure 4.15 Cyclic voltammetry of copper concentrate after being leached in the absence of pyrite for 21.5 hours using a SPCPE electrode in 0.5M H₂SO₄ solution.

After 45 hours of leaching (Figure 4.16), peaks C1 and C4 have disappeared completely, as well as the prewave. Current densities have decreased by about two orders of magnitude from those of the fresh sample.
Figure 4.16 Cyclic voltammetry of copper concentrate after being leached in the absence of pyrite for 45 hours using a SPCPE electrode in 0.5M H₂SO₄ solution.

4.2.4 Electrochemical Behavior of Chalcopyrite Leached in the Presence of Pyrite

Figure 4.17 to Figure 4.20 show voltammograms of chalcopyrite electrodes made from samples taken from a batch leaching test in the presence of pyrite. Comparing them with the voltammogram shown in Figure 4.11 reveals a displacement of peak C1 from 400 mV to less than 200 mV. This indicates the successful separation of pyrite from the leached chalcopyrite, and confirms that the peaks shown in Figure 4.17 to Figure 4.20 are a result of voltammetry on leached chalcopyrite particles only.
Figure 4.17 Cyclic voltammetry of copper concentrate after being leached in the presence of pyrite concentrate #1 for 1.5 hours using a SPCPE electrode in 0.5M H₂SO₄ solution.

After just 1.5 hours of leaching in the presence of pyrite (Figure 4.17), current densities are about one order of magnitude lower than those measured on fresh chalcopyrite. The amount of copper extracted from this sample is comparable to that of the sample leached in the absence of pyrite after 4.5 hours. It is also observed, moving from Figure 4.17 to Figure 4.20, that the cathodic peaks virtually disappear as leaching progresses. On the other hand, most anodic peaks are still visible in Figure 4.18 and Figure 4.19. In Figure 4.20, which shows the voltammogram of a sample from which roughly 90% of the copper has been extracted, the only visible peak is A3. This indicates that chalcopyrite samples leached in the presence of pyrite are more vulnerable to anodic reactions than cathodic reactions. The current density recorded at the maximum
potential on the electrode prepared from chalcopyrite that was leached for 3 hours in the presence of pyrite (Figure 4.18) was 0.06 mA/cm$^2$. This is comparable to the current density of 0.04 mA/cm$^2$ measured on the electrode prepared from chalcopyrite leached in the absence of pyrite for 21.5 hours (Figure 4.15).

In summary, the anodic and cathodic currents of electrodes prepared from samples that were leached in the presence of pyrite showed a significant decrease in current density.

The difference in electrochemical behavior shown in Figure 4.13 to Figure 4.16 and Figure 4.17 to Figure 4.20 is due to the presence of pyrite in the reactor and its catalytic
effect on chalcopyrite leaching. Higher copper extractions cause lower current densities in the subsequent voltammetry.

The disappearance of cathodic peaks C1, C2 and C3 in Figure 4.13 to Figure 4.16 compared to Figure 4.17 to Figure 4.20 could be a sign of a different mechanism being involved in chalcopyrite dissolution. Considering the absence of peak C3 in Figure 4.17 to Figure 4.20 it appears that chalcopyrite follows different reaction pathways in the presence of pyrite (Figure 4.13 to Figure 4.16). The C3 peak relates to chalcopyrite transformation to intermediate copper sulfides such as talnakhite (Cu₉Fe₈S₁₆), mooihoekite (Cu₉Fe₉S₁₆) or bornite (Cu₅FeS₄) as per reactions (R4.6) and (R4.7). The absence of peak C3 in Figure 4.17 to Figure 4.20 can be attributed to the effect of the presence of pyrite in the leach causing the electrode surface to be transformed according to reaction (R4.8). On the other hand, the similarities between Figure 4.13 and Figure 4.17 show that chalcopyrite leaching in both the absence and presence of pyrite follows the same pattern during the first few hours of leaching. However, after a few hours, when the presence of pyrite becomes influential on the leaching mechanism, different behaviors are observed. Figure 4.17 to Figure 4.20 reveals that the reduction of ferric and cupric ions in the potential range of 100 to 200 mV occurs with much less intensity after leaching in the presence of pyrite for 3 hours than after leaching in the absence of pyrite for 9 hours (Figure 4.13 to Figure 4.16). This decrease in intensity continues in the samples taken after longer periods of leaching, and is a direct effect of the presence of pyrite in the leaching reactor, which offers a better surface for ferric reduction. The absence of peak C3 (due to the reduction of chalcopyrite to intermediate copper sulfides) in Figure 4.17 to Figure 4.20 is further evidence of a different mechanism for the dissolution of chalcopyrite in the presence of pyrite. This also shows that ferric reduction does not occur readily on chalcopyrite and pyrite is required to be added to the leaching reactor to offer a more active surface for ferric reduction.
Figure 4.19 Cyclic voltammetry of copper concentrate after being leached in the presence of pyrite concentrate #1 for 4.5 hours using a SPCPE electrode in 0.5M H₂SO₄ solution.

The charge passed during both anodic dissolution (Qₐ) and cathodic reduction (Qₖ) reactions is integrated from the corresponding peaks shown in Figure 4.7 and Figure 4.13. Figure 4.20 shows the ratio of anodic and cathodic charges as a function of leaching time in both the presence and absence of pyrite.
It is clearly shown that when pyrite is present during the leaching of chalcopyrite the relative anodic current increases. This is possibly due to the galvanic effect of pyrite assisting the dissolution of copper from chalcopyrite which is one of the several effects that pyrite has on chalcopyrite leaching. Figure 4.21 shows that in both types of electrodes after the first three hours of leaching, the ratio of anodic to cathodic charges increases with leaching time. However, in samples leached for more than 3 hours in the absence of pyrite this ratio begins to fall. This indicates the passivation of chalcopyrite. On the other hand, in samples leached in the presence of pyrite the ratio of anodic to cathodic charges increases throughout the leach cycle, which indicates a more active electrode. The exception is the measurement after 9 hours of leaching, at which point
an abrupt decline is observed relating to a sharp decrease in the anodic charge due to the depletion of chalcopyrite in the sample.

Figure 4.21  Ratio of anodic and cathodic charges calculated by integration of cyclic voltammograms.

Figure 4.22, compares the peak intensities of ferric reduction on fresh chalcopyrite and leached chalcopyrite. These data have been extracted from Figure 4.13 to Figure 4.16. The correlation between the current density of ferric reduction and leaching time is interesting because, as the leaching time increases from 0 to 45 hours, the magnitude of the ferric reduction peak becomes smaller. In other words, in all four electrodes that were prepared consecutively from leached chalcopyrite the ability of chalcopyrite to reduce ferric ions is shown to be steadily declining with increased leaching time.
In order to eliminate a major source of uncertainty in the method used to measure the current density of ferric reduction, attention needs to be drawn to the fact that the total surface area of the unleached chalcopyrite is decreasing with time as the chalcopyrite particles are shrinking. However, in the preparation of the electrodes the same mass of residue is used each time. This causes an increase in the total number of particles in each successive electrode. Thus, considering that only a small portion of the copper dissolves, the surface area remains roughly the same in successive electrodes relative to the initial mass or might even increase slightly. Considering these factors, it is shown that the magnitude of the cathodic peak is falling by orders of magnitude from one
electrode to the next. Therefore, the decrease in current density truly represents a steady decrease in the ability of partially leached chalcopyrite particles to reduce ferric.

In other words, the rate of ferric reduction on chalcopyrite decreases logarithmically with time spent in the leaching reactor.

The electrodes prepared from samples leached in the presence of pyrite also lost their ability to reduce ferric, showing that they too were passivated.

The steady and dramatic cathodic passivation of chalcopyrite during leaching is truly observed. It cannot be said conclusively that pyrite fulfills this role on behalf of chalcopyrite. However, it is obvious from the results presented in Figure 4.22 that chalcopyrite cannot fulfill this role on its own behalf. Since in order for an electrochemical leach to occur there has to be a cathodic half-cell reaction, it can be concluded that pyrite is acting as the cathode in the galvanically-assisted leaching process.

Finally, Figure 4.23 compares the ferric reduction peak intensities on two different pyrite samples. It is shown that a higher current density is measured on the surface of the electrode prepared from pyrite #1. This result corroborates earlier findings showing faster leaching results when pyrite #1 was used Figure 4.1, and further suggests a galvanic interaction between the two minerals.
Figure 4.23  Cathodic current density of ferric reduction on pyrite samples #1 and #4 (solution: 0.5 M sulfuric acid and 0.01 M ferric sulfate).
CHAPTER 5: Electrochemical Characterization of Natural Pyrite Using Single Particle Microelectrode Technique

5.1 Cyclic Voltammetry (CV) Employing Micro Electrode Technique

The cyclic voltammograms generated for pyrites #1 and #4 are depicted in Figure 5.1 and Figure 5.2. The scan is initiated from the open circuit potential (OCP) of pyrite in the anodic direction. Similar to the results recorded using SPCPE technique, three anodic current peaks A1, A2 and A3 are observed. During the cathodic scan, two cathodic peaks C1 and C2 are recorded. This similarity of recorded voltammograms using both techniques shows the reliability of those techniques.

![Cyclic voltammogram showing the oxidation and reduction of Pyrite #1 using a microelectrode in 0.5M H₂SO₄ solution.](image)

Figure 5.1 Cyclic voltammogram showing the oxidation and reduction of Pyrite #1 using a microelectrode in 0.5M H₂SO₄ solution.
Figure 5.2  Cyclic voltammogram showing the oxidation and reduction of Pyrite #4 using a microelectrode in 0.5M H$_2$SO$_4$ solution.

Voltammetry of four different pyrites showed similar behavior, except for peak C1 for which significantly higher current densities were recorded on the surface of pyrite #1. Figure 5.3 compares the peak intensities recorded on all four pyrites. The most likely explanation for this observed difference in the peak height is the faster kinetics of ferric reduction on the surface of pyrite #1. This result also accords with my earlier observations, which showed faster leaching results when pyrite #1 was used Figure 4.1.
5.2 Polarization

The impedance measurements were commenced with measurement of a steady-state polarization curve of pyrite electrodes. Orazem and Tribollet (2008) highlighted the need to measure the steady-state polarization curve as a guide for selection of appropriate perturbation amplitude and to provide initial hypotheses for model development. The impedance measurements can then be performed at selected points on the polarization curve to explore the characteristics of the system.

Figure 5.4 shows polarization curves for an electrode of pyrite #1 at scan rates of 0.05, 0.5, 5, and 50 mV s\(^{-1}\) and a carbon microelectrode without being in touch with any pyrite particle. Typically, applying a slower scan rate will reveal a closer approximation
to steady-state electrode behavior. In the case of the present study, the polarization current decreases with decreasing scan rate; similar results have been reported previously by Ghahremaninezhad et al. (2010) and Warren et al. (1982) for CuFeS₂ in 0.5 M and 1 M sulfuric acid solutions respectively. In the cathodic part of the polarization curve, the curves show more similar behavior which indicates that the initial sample surfaces have similar properties. No clear active-passive behavior was observed during the course of recording the polarization curves. Potentiodynamic curve measured on the carbon electrode shows that the current measured on its surface when it is not connected to any particle is more than 4 orders of magnitude smaller than what is measured on the surface of pyrite. Therefore, considering it as an inert electrode would be a valid assumption for the rest of experiments.
5.3 Electrochemical Impedance Spectroscopy (EIS) Study of Pyrite

EIS studies on pyrite single particle microelectrodes were conducted on four different pyrite samples at 420 mV vs. SCE, which is the optimum potential for the pyrite-assisted leaching of chalcopyrite. The resulting impedance spectra can be quite complex, and generally their characteristics change with the applied potential. The impedance spectra of one pyrite sample are shown in Figure 5.7 to Figure 5.11.

Since impedance is a complex quantity, the two sets of traditional methods of data representation are used to show the results for each measurement: the Nyquist plot, in which the negative imaginary component of impedance (−Z″) is given as a function of
the real component \( (Z') \), and the Bode plot, in which the magnitude of both the absolute values of the impedance \( |Z| \) and its argument, the phase angle \( \varphi \), are given as a function of frequency.

In all impedance spectra, the measured data points and the fitted curves obtained using equivalent analog circuit models for the pyrite/solution interface are shown, by various symbols, as discrete points.

### 5.3.1 Model Development

To investigate the properties of the pyrite/solution interface and the associated electrochemical processes, it was necessary to model the datasets with equivalent circuit models. The system is more complicated than the simplistic, idealized model of picturing the redox reaction mechanisms as an electrode/electrolyte interface due to the fact that the interfaces are not smooth and are filled with structured defects. Additionally, the influence of different impurities on the local charge transfer should not be underestimated.

In cases where the data are simple, an impedance spectroscopist can become quite adept at intuitively visualizing equivalent circuits from Nyquist and Bode plots. However, as the complication of the data increases such intuitive visualization of circuits can become a cumbersome task. Thus, employing a computer to model the equivalent circuit of electrode/electrolyte becomes a necessity.

When using equivalent circuits to simulate a process, one needs to be aware that more than one equivalent circuit may fit a particular set of experimental data. The best example is the three mathematically equivalent circuits often referred to as Voigt, Maxwell and Ladder circuits. In those circuits, two time constants can yield the same impedance response for all frequencies when their component values are properly related. Thus, in the proposed model, each circuit component should come from a physical process in the electrochemical cell and should have characteristic impedance behavior. Although powerful numerical analysis software are available to fit the spectra to give the best values for equivalent circuit parameters, analysis of the impedance data
can still be troublesome. Ergo, a good knowledge of electrochemical processes such as Warburg diffusion, adsorption redox process, crystal defects or semiconductive properties of the electrode and the effect of different doping elements is necessary.

Eight approaches are considered in this study to develop models to analyze the measured impedance spectra:

- The proposed equivalent circuit is made as simple as possible to represent the electrochemical system and to give the best possible fit between the impedance of the model and the measured impedance of the system.
- The equivalent circuit model is developed from physical grounds. In other words, a correspondence between physical models and electrical circuit is identifiable.
- Kramers-Kronig transformations are employed as a test for verification of electrochemical impedance spectroscopy data. The four conditions of linearity, causality, stability and finiteness are satisfied for spectra complying with these transformations.
- A qualitative comparison of the shape of the observed spectrum with the expected spectrum on the basis of various models is considered. From such a comparison, selection of the most appropriate model becomes possible. Some parameters could be estimated based on the value of impedance at low- or high-frequency limits. For instance, the solution resistance can be estimated at the interception of the Nyquist plot with the x-axis at high frequencies. The charge transfer resistance may be determined from the diameter of the semicircle in the same plot.
- Several equivalent circuits modeling pyrite/solution interface suggested by previous researchers published in scientific journals are considered.
- A statistical procedure is used to determine the model which best describes the measured spectra. Experimental errors and incomplete spectra due to instrumental limitations cause difficulties in analysis of the impedance spectra. Minimizing the variance between experimental and estimated values is used to match the experimental impedances with estimated values for all the frequencies.
In order to estimate the best model for the system within chosen model structure, it is validated statistically. Among various statistical methods the classical Pearson correlation coefficient is chosen as a measure of the strength of linear dependence between all parameters of the model. Since the number of parameters in the model is large this cross-validation prohibits overfitting. Correlation coefficient matrices calculated from covariance matrices and standard deviation matrices are shown for each model. This validation allows the researcher to quickly identify problems in the model as well as increases the understanding of the abilities and limitations of the model. It also assists the researcher to fine-tune the model.

The best equivalent model is the one which best predicts any imposed change on the system. In order to select a particular model an additional experiment involving the addition of nanoparticles to the pyrite electrodes is performed.

Equivalent electrical circuits consisting of lumped and distributed elements were used to model the impedance spectra. The EIS spectra were analyzed using a Boukamp equivalent circuit program (Boukamp, 1989).

After several attempts to fit the experimental impedance datasets to various models shown in Figure 5.5 and Figure 5.6, the equivalent circuit \( R_{sol}(R_{ct}Q)(C_{sc}R_{ss}) \) provided the best fit to the EIS data (Figure 5.5).

![Figure 5.5 Equivalent analog circuit of pyrite/solution interface at 420 mV \( R_{sol}(R_{ct}Q)(C_{sc}R_{ss}) \).](image-url)
Figure 5.7 shows the measured and fit using equivalent circuit model $R_{so}(R_{ct}Q)(C_{sc}R_{ss})$. In order to test if the proposed equivalent circuit model here gives the best fit, other models shown in Figure 5.6 are also considered in this study. The results of modeling with these models are shown in Figure 5.7 to Figure 5.13 and the corresponding analyzed data are presented in Table 5.1 to Table 5.14.

First the equivalent circuit used by Pang et al. (1990) and Lin and Say (1999) to model pyrite impedance spectra was considered. This equivalent circuit can intuitively be recognized not to give the proper fit by just considering the shape of the Nyquist plot since these models give a depressed semicircle.

Then, a simplified version (Figure 5.6b) of the equivalent circuit proposed in this thesis, (Figure 5.5) is used to model the data. The results of using a single time constant circuit $R_{so}(R_{ct}Q)$ are presented in Figure 5.8,Table 5.3 and Table 5.4. It is obvious from Figure 5.8 that this is not a good fit. Additionally, the fact that value of $\chi^2$ did not increase by an order of magnitude, confirms that this model was not a good fit.
The next model to consider is the one used by Velasquez et al. (2005). The equivalent circuit used by Velasquez et al. (2005), \( R_1(Q_1(R_2(Q_2R_3)(R_4L))) \), does not show a good fit with the impedance data acquired in this study. This can be concluded from the high values of relative standard errors reported in Table 5.5 for three of the resistances and the inductance. The dependence of several model elements, as evidenced by the values of correlation coefficients which are nearly one in Table 5.6 (the best examples are the correlation between \( R_2 \) and CPE, \( R_2 \) and \( R_4 \) and \( R_4 \) and CPE). A correlation value greater than 0.8 is considered as a strong correlation. As it is shown the correlation matrix is symmetric as the correlation between \( X_i \) and \( X_j \) is the same as the correlation between \( X_j \) and \( X_i \). The diagonal of this matrix consists of ones which proves the calculation is correct because these are the correlations between each variable and itself. The correlation between \( Q-Y_0 \) and \( Q-n \) in an ideal system should equal negative...
one since they belong to one parameter. A negative sign here implies that all data points lie on a line for which \( Q-Y_0 \) decreases as \( Q-n \) increases to keep the value of Constant Phase Element (CPE) constant. For details on CPE readers are referred to section 5.3.2.3.

This equivalent circuit is probably valid at different conditions such as the electrodes being electrochemically processed prior to EIS, different applied potential or a different electrolyte.

The results of applying the equivalent circuit used by Lehner et al. (2008) on the impedance data acquired in this study are presented in Figure 5.10, Table 5.7 and Table 5.8. Despite the good fit shown in Figure 5.10, this model is not considered to be the best model for the data presented here, based on the following six reasons. The introduction of the extraneous elements did not improve the value of \( \chi^2 \). Boukamp (1989) recommends that the value of \( \chi^2 \) should decrease by tenfold if a new circuit element is introduced into the circuit model. The relative standard error in the value of Warburg impedance and the first capacitance are not in the acceptable range. The correlation coefficient matrix shows a dependence of the last resistance to the Warburg impedance. Placing the Warburg impedance in the inner circuit does give the best fit, however the typical physical interpretation of Warburg impedance does not agree with this (section 5.3.2.4). As well three time constants were not observed in the spectra as suggested by the Lehner et al. (2008) model. Finally, this is not the simplest equivalent circuit as there are other equally likely solutions.

The equivalent circuit used by Lehner et al. (2008) was simplified by eliminating the inner circuit and relocating the Warburg impedance close to charge transfer resistance. This modified version as shown in Figure 5.6d is used in analyzing the EIS data. However, the results do not provide an improvement as shown in Figure 5.11, Table 5.9 and Table 5.10. The calculated Warburg impedance is notably large and the physical meaning of it is not clear. In addition the shape of the acquired spectra does not infer a mass transport control mechanism. The relative standard error of the Warburg impedance is too high to be considered reliable. Finally, the correlation coefficient
matrix shows a dependent model making it invalid. Warburg impedance in both cases showed a strong correlation to other circuit elements making it unnecessary in the model.
Figure 5.7 Nyquist and Bode plots showing the fit of $R_{\text{sol}}(R_{\text{ct}}Q)(C_{\text{sc}}R_{\text{ss}})$ model and impedance error measurement of Pyrite sample P#1-1 using a microelectrode (solution 0.5M H$_2$SO$_4$, 0.005M Fe$_2$(SO$_4$)$_3$ and 0.005M Fe(SO$_4$)$_3$).
Figure 5.8 Nyquist and Bode plots showing the fit of $R_1(R_2Q_1)$ model and impedance error measurement of Pyrite sample P#1-1 using a microelectrode (solution 0.5M H$_2$SO$_4$, 0.005M Fe$_2$(SO$_4$)$_3$ and 0.005M Fe(SO$_4$)).
Figure 5.9  Nyquist and Bode plots showing the fit of $R_1(Q_1(R_2(Q_2R_3)(R_4L)))$ model and impedance error measurement of Pyrite sample P#1-1 using a microelectrode (solution 0.5M H$_2$SO$_4$, 0.005M Fe$_2$(SO$_4$)$_3$ and 0.005M Fe(SO$_4$)).
Figure 5.10 Nyquist and Bode plots showing the fit of $R_1(R_2Q_1)(C_1(R_3(C_2(R_4W))))$ model and impedance error measurement of Pyrite sample P#1-1 using a microelectrode (solution 0.5M H$_2$SO$_4$, 0.005M Fe$_2$(SO$_4$)$_3$ and 0.005M Fe(SO$_4$).
Figure 5.11 Nyquist and Bode plots showing the fit of \( R_1(Q_1(R_2W))(C_1R_3) \) model and impedance error measurement of Pyrite sample P#1-1 using a microelectrode (solution 0.5M \( \text{H}_2\text{SO}_4 \), 0.005M \( \text{Fe}_2(\text{SO}_4)_3 \) and 0.005M Fe(\( \text{SO}_4 \)).
Table 5.1  Values of elements of equivalent circuit $R_{sol}(R_{ct}Q)(C_{sc}R_{ss})$ for sample P#1-1. Measurement errors in impedance data are smaller than 5%.

<table>
<thead>
<tr>
<th></th>
<th>$R_{sol} (\Omega cm^2)$</th>
<th>$R_{ct} (\Omega cm^2)$</th>
<th>$Q-Yo (\Omega s^{-n})$</th>
<th>$Q-n$</th>
<th>$C_{sc}(F/cm^2)$</th>
<th>$R_{ss} (\Omega cm^2)$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P#1-1</td>
<td>8.3</td>
<td>219.2</td>
<td>$3 \times 10^{-4}$</td>
<td>0.7</td>
<td>$4.5 \times 10^{-3}$</td>
<td>766</td>
<td>$2.11 \times 10^{-3}$</td>
</tr>
<tr>
<td>RSE%</td>
<td>1.3</td>
<td>2</td>
<td>4.7</td>
<td>1</td>
<td>3.1</td>
<td>5.6</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2  Correlation matrix of elements of equivalent circuit $R_{sol}(R_{ct}Q)(C_{sc}R_{ss})$ of sample P#1-1.

<table>
<thead>
<tr>
<th></th>
<th>$R_{sol}$</th>
<th>$R_{ct}$</th>
<th>$Q-Yo$</th>
<th>$Q-n$</th>
<th>$C_{sc}$</th>
<th>$R_{ss}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{sol}$</td>
<td>1.00</td>
<td>0.24</td>
<td>-0.39</td>
<td>0.48</td>
<td>-0.12</td>
<td>0.03</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>0.24</td>
<td>1.00</td>
<td>-0.61</td>
<td>0.58</td>
<td>-0.52</td>
<td>0.23</td>
</tr>
<tr>
<td>$Q-Yo$</td>
<td>-0.39</td>
<td>-0.61</td>
<td>1.00</td>
<td>-0.96</td>
<td>0.33</td>
<td>-0.09</td>
</tr>
<tr>
<td>$Q-n$</td>
<td>0.48</td>
<td>0.58</td>
<td>-0.96</td>
<td>1.00</td>
<td>-0.31</td>
<td>0.09</td>
</tr>
<tr>
<td>$C_{sc}$</td>
<td>-0.12</td>
<td>-0.52</td>
<td>0.33</td>
<td>-0.31</td>
<td>1.00</td>
<td>-0.12</td>
</tr>
<tr>
<td>$R_{ss}$</td>
<td>0.03</td>
<td>0.23</td>
<td>-0.09</td>
<td>0.09</td>
<td>-0.12</td>
<td>1.00</td>
</tr>
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</table>

Table 5.3  Values of elements of equivalent circuit $R_{sol}(R_{ct}Q)$ for sample P#1-1. Measurement errors in impedance data are smaller than 23.5%.

<table>
<thead>
<tr>
<th></th>
<th>$R_{sol} (\Omega cm^2)$</th>
<th>$R_{ct} (\Omega cm^2)$</th>
<th>$Q-Yo (\Omega s^{-n})$</th>
<th>$Q-n$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P#1-1</td>
<td>6.8</td>
<td>791</td>
<td>$1.1 \times 10^{-3}$</td>
<td>0.51</td>
<td>$5.51 \times 10^{-2}$</td>
</tr>
<tr>
<td>RSE%</td>
<td>9.3</td>
<td>16.8</td>
<td>13.5</td>
<td>4.45</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4  Correlation matrix of elements of equivalent circuit $R_{sol}(R_{ct}Q)$ of sample P#1-1.

<table>
<thead>
<tr>
<th></th>
<th>$R_{sol}$</th>
<th>$R_{ct}$</th>
<th>$Q-Yo$</th>
<th>$Q-n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{sol}$</td>
<td>1.00</td>
<td>0.33</td>
<td>-0.44</td>
<td>0.61</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>0.33</td>
<td>1.00</td>
<td>-0.73</td>
<td>0.67</td>
</tr>
<tr>
<td>$Q-Yo$</td>
<td>-0.44</td>
<td>-0.73</td>
<td>1.00</td>
<td>-0.91</td>
</tr>
<tr>
<td>$Q-n$</td>
<td>0.61</td>
<td>0.67</td>
<td>-0.91</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Table 5.5  Values of elements of equivalent circuit $R_1(Q_1(R_2(Q_2R_3)(R_4L)))$ for sample P#1-1. Measurement errors in impedance data are smaller than 4.6%.

<table>
<thead>
<tr>
<th></th>
<th>$R_1$ ($\Omega \text{cm}^2$)</th>
<th>$Q_1\cdot Y_0$ ($\Omega\text{s}^{-n}$)</th>
<th>$Q_1\cdot n$</th>
<th>$R_2$ ($\Omega \text{cm}^2$)</th>
<th>$Q_2\cdot Y_0$ ($\Omega\text{s}^{-n}$)</th>
<th>$Q_2\cdot n$</th>
<th>$R_3$ ($\Omega \text{cm}^2$)</th>
<th>$R_4$ ($\Omega \text{cm}^2$)</th>
<th>$L$ (H)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P#1-1</td>
<td>8.3</td>
<td>$3 \times 10^{-4}$</td>
<td>0.7</td>
<td>0.03</td>
<td>$3 \times 10^{-3}$</td>
<td>1</td>
<td>837.9</td>
<td>237.7</td>
<td>5417</td>
<td>$2.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>RSE%</td>
<td>1.3</td>
<td>5.6</td>
<td>1.2</td>
<td>$2.7 \times 10^7$</td>
<td>97</td>
<td>6</td>
<td>176</td>
<td>3447</td>
<td>9236</td>
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Table 5.6  Correlation matrix of elements of equivalent circuit $R_1(Q_1(R_2(Q_2R_3)(R_4L)))$ of sample P#1-1.

<table>
<thead>
<tr>
<th></th>
<th>$R_1$</th>
<th>$Q_1\cdot Y_0$</th>
<th>$Q_1\cdot n$</th>
<th>$R_2$</th>
<th>$Q_2\cdot Y_0$</th>
<th>$Q_2\cdot n$</th>
<th>$R_3$</th>
<th>$R_4$</th>
<th>$L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$</td>
<td>1.00</td>
<td>-0.57</td>
<td>0.61</td>
<td>-0.41</td>
<td>-0.24</td>
<td>-0.38</td>
<td>-0.31</td>
<td>-0.28</td>
<td>-0.27</td>
</tr>
<tr>
<td>$Q_1\cdot Y_0$</td>
<td>-0.57</td>
<td>1.00</td>
<td>-0.99</td>
<td>0.86</td>
<td>0.51</td>
<td>0.82</td>
<td>0.69</td>
<td>0.66</td>
<td>0.56</td>
</tr>
<tr>
<td>$Q_1\cdot n$</td>
<td>0.61</td>
<td>-0.99</td>
<td>1.00</td>
<td>-0.82</td>
<td>-0.49</td>
<td>-0.77</td>
<td>-0.65</td>
<td>-0.61</td>
<td>-0.54</td>
</tr>
<tr>
<td>$R_2$</td>
<td>-0.41</td>
<td>0.86</td>
<td>-0.82</td>
<td>1.00</td>
<td>0.71</td>
<td>0.93</td>
<td>0.75</td>
<td>0.92</td>
<td>0.71</td>
</tr>
<tr>
<td>$Q_2\cdot Y_0$</td>
<td>-0.24</td>
<td>0.51</td>
<td>-0.49</td>
<td>0.71</td>
<td>1.00</td>
<td>0.40</td>
<td>0.07</td>
<td>0.85</td>
<td>0.88</td>
</tr>
<tr>
<td>$Q_2\cdot n$</td>
<td>-0.38</td>
<td>0.82</td>
<td>-0.77</td>
<td>0.93</td>
<td>0.40</td>
<td>1.00</td>
<td>0.94</td>
<td>0.76</td>
<td>0.43</td>
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<td>$R_3$</td>
<td>-0.31</td>
<td>0.69</td>
<td>-0.65</td>
<td>0.75</td>
<td>0.07</td>
<td>0.94</td>
<td>1.00</td>
<td>0.52</td>
<td>0.16</td>
</tr>
<tr>
<td>$R_4$</td>
<td>-0.28</td>
<td>0.66</td>
<td>-0.61</td>
<td>0.92</td>
<td>0.85</td>
<td>0.76</td>
<td>0.52</td>
<td>1.00</td>
<td>0.83</td>
</tr>
<tr>
<td>$L$</td>
<td>-0.27</td>
<td>0.56</td>
<td>-0.54</td>
<td>0.71</td>
<td>0.88</td>
<td>0.43</td>
<td>0.16</td>
<td>0.83</td>
<td>1.00</td>
</tr>
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</table>
Table 5.7  Values of elements of equivalent circuit $R_1(R_2Q_1)(C_1(R_3(C_2(R_4W))))$ for sample P#1-1. Measurement errors in impedance data are smaller than 4.3%.

<table>
<thead>
<tr>
<th></th>
<th>$R_1$ (Ωcm$^2$)</th>
<th>$R_2$ (Ωcm$^2$)</th>
<th>$Q_1-Y_0$ (Ωs$^{-n}$)</th>
<th>$Q_1-n$</th>
<th>$C_1$ (Fcm$^{-2}$)</th>
<th>$R_3$ (Ωcm$^2$)</th>
<th>$C_2$ (Fcm$^{-2}$)</th>
<th>$R_4$ (Ωcm$^2$)</th>
<th>$W$ (Ωs$^{-0.5}$)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P#1-1</td>
<td>8.1</td>
<td>214.7</td>
<td>2.8×10$^{-4}$</td>
<td>0.72</td>
<td>2.5×10$^{-5}$</td>
<td>0.73</td>
<td>4×10$^{-3}$</td>
<td>761.2</td>
<td>2.9×10$^5$</td>
<td>1.86×10$^{-3}$</td>
</tr>
<tr>
<td>RSE%</td>
<td>1.6</td>
<td>2.1</td>
<td>5.5</td>
<td>1.3</td>
<td>52.78</td>
<td>33.5</td>
<td>4.5</td>
<td>9.6</td>
<td>1.5×10$^9$</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.8  Correlation matrix of elements of equivalent circuit $R_1(R_2Q_1)(C_1(R_3(C_2(R_4W))))$ of sample P#1-1.

<table>
<thead>
<tr>
<th>P#1-1</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$Q_1-Y_0$</th>
<th>$Q_1-n$</th>
<th>$C_1$</th>
<th>$R_3$</th>
<th>$C_2$</th>
<th>$R_4$</th>
<th>$W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$</td>
<td>1.00</td>
<td>0.12</td>
<td>-0.16</td>
<td>0.19</td>
<td>0.66</td>
<td>-0.23</td>
<td>-0.10</td>
<td>-0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>$R_2$</td>
<td>0.12</td>
<td>1.00</td>
<td>-0.69</td>
<td>0.66</td>
<td>-0.04</td>
<td>0.39</td>
<td>-0.56</td>
<td>-0.38</td>
<td>0.31</td>
</tr>
<tr>
<td>$Q_1-Y_0$</td>
<td>-0.16</td>
<td>-0.69</td>
<td>1.00</td>
<td>-0.96</td>
<td>0.06</td>
<td>-0.55</td>
<td>0.38</td>
<td>0.23</td>
<td>-0.20</td>
</tr>
<tr>
<td>$Q_1-n$</td>
<td>0.19</td>
<td>0.66</td>
<td>-0.96</td>
<td>1.00</td>
<td>-0.05</td>
<td>0.65</td>
<td>-0.36</td>
<td>-0.21</td>
<td>0.19</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.66</td>
<td>-0.04</td>
<td>0.06</td>
<td>-0.05</td>
<td>1.00</td>
<td>-0.26</td>
<td>-0.04</td>
<td>0.02</td>
<td>-0.01</td>
</tr>
<tr>
<td>$R_3$</td>
<td>-0.23</td>
<td>0.39</td>
<td>-0.55</td>
<td>0.65</td>
<td>-0.26</td>
<td>1.00</td>
<td>-0.18</td>
<td>-0.11</td>
<td>0.10</td>
</tr>
<tr>
<td>$C_2$</td>
<td>-0.10</td>
<td>-0.56</td>
<td>0.38</td>
<td>-0.36</td>
<td>-0.04</td>
<td>-0.18</td>
<td>1.00</td>
<td>0.68</td>
<td>-0.76</td>
</tr>
<tr>
<td>$R_4$</td>
<td>-0.03</td>
<td>-0.38</td>
<td>0.23</td>
<td>-0.21</td>
<td>0.02</td>
<td>-0.11</td>
<td>0.68</td>
<td>1.00</td>
<td>-0.84</td>
</tr>
<tr>
<td>$W$</td>
<td>0.03</td>
<td>0.31</td>
<td>-0.20</td>
<td>0.19</td>
<td>-0.01</td>
<td>0.10</td>
<td>-0.76</td>
<td>-0.84</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Table 5.9  Values of elements of equivalent circuit $R_1(Q_1(R_2W))(C_1R_3)$ for sample P#1-1. Measurement errors in impedance data are smaller than 4.6%.

<table>
<thead>
<tr>
<th></th>
<th>$R_1$ (Ωcm$^2$)</th>
<th>$Q_1-Y_o$ (Ωs$^{-n}$)</th>
<th>$Q_1-n$</th>
<th>$R_2$ (Ωcm$^2$)</th>
<th>$W$ (Ωs$^{0.5}$)</th>
<th>$C_1$ (Fcm$^2$)</th>
<th>$R_3$ (Ωcm$^2$)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P#1-1</td>
<td>8.3</td>
<td>3×10$^{-4}$</td>
<td>0.7</td>
<td>219</td>
<td>3.4×10$^{13}$</td>
<td>4.5×10$^{-3}$</td>
<td>766</td>
<td>2.1×10$^{-3}$</td>
</tr>
<tr>
<td>RSE%</td>
<td>1.3</td>
<td>6.2</td>
<td>1.3</td>
<td>3.8</td>
<td>9.3×10$^{16}$</td>
<td>10.6</td>
<td>9.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.10  Correlation matrix of elements of equivalent circuit $R_1(Q_1(R_2W))(C_1R_3)$ of sample P#1-1.

<table>
<thead>
<tr>
<th></th>
<th>$R_1$</th>
<th>$Q_1-Y_o$</th>
<th>$Q_1-n$</th>
<th>$R_2$</th>
<th>$W$</th>
<th>$C_1$</th>
<th>$R_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$</td>
<td>1.00</td>
<td>-0.44</td>
<td>0.51</td>
<td>-0.32</td>
<td>0.23</td>
<td>0.18</td>
<td>0.20</td>
</tr>
<tr>
<td>$Q_1-Y_o$</td>
<td>-0.44</td>
<td>1.00</td>
<td>-0.97</td>
<td>0.79</td>
<td>-0.63</td>
<td>-0.53</td>
<td>-0.55</td>
</tr>
<tr>
<td>$Q_1-n$</td>
<td>0.51</td>
<td>-0.97</td>
<td>1.00</td>
<td>-0.74</td>
<td>0.57</td>
<td>0.48</td>
<td>0.51</td>
</tr>
<tr>
<td>$R_2$</td>
<td>-0.32</td>
<td>0.79</td>
<td>-0.74</td>
<td>1.00</td>
<td>-0.84</td>
<td>-0.72</td>
<td>-0.75</td>
</tr>
<tr>
<td>$W$</td>
<td>0.23</td>
<td>-0.63</td>
<td>0.57</td>
<td>-0.84</td>
<td>1.00</td>
<td>0.95</td>
<td>0.81</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.18</td>
<td>-0.53</td>
<td>0.48</td>
<td>-0.72</td>
<td>0.95</td>
<td>1.00</td>
<td>0.75</td>
</tr>
<tr>
<td>$R_3$</td>
<td>0.20</td>
<td>-0.55</td>
<td>0.51</td>
<td>-0.75</td>
<td>0.81</td>
<td>0.75</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Differences were observed in the shape of Nyquist and Bode plots obtained from pyrite samples #2, #3 and #4 with respect to those of pyrite #1. The equivalent circuit used to fit pyrite #1, \( R_{sol}(R_{ct}Q)(R_{ss}C_{sc}) \), was used for other pyrite samples (Figure 5.12, Table 5.11 and Table 5.12). A good fit can be seen between the modeled data and the measured spectra. The values reported in Table 5.11 for the elements of the second time constant include about 45% relative standard error. Based on the high error associated with this element and given the shape of the Nyquist and Bode plots of these samples did not show a clear second time constant, the last RC was eliminated from the circuit. The results are shown in Figure 5.13, Table 5.13 and Table 5.14. A good fit can be observed in the Nyquist and Bode plots. The values for the first three elements have not change and the relative standard errors are low. The value of \( \chi^2 \) has changed from \( 2.5 \times 10^{-3} \) to \( 2.7 \times 10^{-3} \), showing a negligible increase. Because the inclusion or elimination of additional circuit elements does not substantially improve the quality of the fit (would expect at least a tenfold difference in the value of \( \chi^2 \) for the inclusion of a meaningful element) the simpler circuit model is chosen based on the principle of parsimony.

The spectra of three pyrite samples from pyrite#1, #2, #3 and #4 with calculated fit using equivalent circuit are presented in Figure 5.14 to Figure 5.17 to show how good are the fit.

The spectra presented in Figure 5.14 to Figure 5.17 are representative of the vast majority of the particles examined from the respective pyrite samples. A small fraction (<10 %) of the spectra obtained display differing characteristics, these could not be satisfactorily modeled by any equivalent circuit containing physically meaningful elements. This could be due to gangue minerals or other sulfide minerals mixed with the pyrite concentrates.
Figure 5.12 Nyquist and Bode plots showing the fit of $R_{sol}(R_{ct}Q)(R_{ss}C_{sc})$ model and impedance error measurement of pyrite sample P#3-3 using a microelectrode (solution 0.5M $H_2SO_4$, 0.005M $Fe_2(SO_4)_3$ and 0.005M $Fe(SO_4)$. 

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Figure 5.13 Nyquist and Bode plots showing the fit of $R_{sol}(R_{cf}Q)$ model and impedance error measurement of pyrite sample P#3-3 using a microelectrode (solution 0.5M H$_2$SO$_4$, 0.005M Fe$_2$(SO$_4$)$_3$ and 0.005M Fe(SO$_4$)$_3$).
Table 5.11  Values of elements of equivalent circuit $R_{\text{sol}}(R_{\text{ct}}Q)(R_{\text{ss}}C_{\text{sc}})$ for sample P#3-3. Measurement errors in impedance data are smaller than 5%.

<table>
<thead>
<tr>
<th></th>
<th>$R_{\text{sol}}$(Ωcm$^2$)</th>
<th>$R_{\text{ct}}$(Ωcm$^2$)</th>
<th>Q-Yo ($\Omega s^n$)</th>
<th>Q-n</th>
<th>$C_{\text{sc}}$(Fcm$^{-2}$)</th>
<th>$R_{\text{ss}}$(Ωcm$^2$)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P#3-3</td>
<td>13.3</td>
<td>1.63×10$^4$</td>
<td>5×10$^{-5}$</td>
<td>0.66</td>
<td>8.4×10$^{-6}$</td>
<td>3</td>
<td>2.46×10$^{-3}$</td>
</tr>
<tr>
<td>RSE%</td>
<td>2.5</td>
<td>2.8</td>
<td>2.3</td>
<td>0.7</td>
<td>44</td>
<td>46</td>
<td>46</td>
</tr>
</tbody>
</table>

Table 5.12  Correlation matrix of elements of equivalent circuit $R_{\text{sol}}(R_{\text{ct}}Q)(R_{\text{ss}}C_{\text{sc}})$ of sample P#3-3.

<table>
<thead>
<tr>
<th></th>
<th>$R_{\text{sol}}$</th>
<th>$R_{\text{ct}}$</th>
<th>Q-Yo</th>
<th>Q-n</th>
<th>$C_{\text{sc}}$</th>
<th>$R_{\text{ss}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P#3-3</td>
<td>1.00</td>
<td>0.19</td>
<td>-0.29</td>
<td>0.37</td>
<td>0.26</td>
<td>-0.24</td>
</tr>
<tr>
<td>$R_{\text{sol}}$</td>
<td>1.00</td>
<td>0.19</td>
<td>-0.33</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{\text{ct}}$</td>
<td>0.19</td>
<td>1.00</td>
<td>-0.59</td>
<td>0.56</td>
<td>-0.22</td>
<td>-0.32</td>
</tr>
<tr>
<td>Q-Yo</td>
<td>-0.29</td>
<td>-0.59</td>
<td>1.00</td>
<td>-0.90</td>
<td>0.35</td>
<td>0.49</td>
</tr>
<tr>
<td>Q-n</td>
<td>0.37</td>
<td>0.56</td>
<td>-0.90</td>
<td>1.00</td>
<td>-0.44</td>
<td>-0.70</td>
</tr>
<tr>
<td>$C_{\text{sc}}$</td>
<td>0.26</td>
<td>-0.22</td>
<td>0.35</td>
<td>-0.44</td>
<td>1.00</td>
<td>0.37</td>
</tr>
<tr>
<td>$R_{\text{ss}}$</td>
<td>-0.24</td>
<td>-0.32</td>
<td>0.49</td>
<td>-0.70</td>
<td>0.37</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 5.13  Values of elements of equivalent circuit $R_{\text{sol}}(R_{\text{ct}}Q)$ for sample P#3-3. Measurement errors in impedance data are smaller than 5.2%.

<table>
<thead>
<tr>
<th></th>
<th>$R_{\text{sol}}$(Ωcm$^2$)</th>
<th>$R_{\text{ct}}$(Ωcm$^2$)</th>
<th>Q-Yo ($\Omega s^n$)</th>
<th>Q-n</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P#3-3</td>
<td>13.3</td>
<td>1.67×10$^5$</td>
<td>5×10$^{-5}$</td>
<td>0.65</td>
<td>2.7×10$^{-3}$</td>
</tr>
<tr>
<td>RSE%</td>
<td>2.3</td>
<td>2.86</td>
<td>2</td>
<td>0.47</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.14  Correlation matrix of elements of equivalent circuit $R_{\text{sol}}(R_{\text{ct}}Q)$ of sample P#3-3.

<table>
<thead>
<tr>
<th></th>
<th>$R_{\text{sol}}$</th>
<th>$R_{\text{ct}}$</th>
<th>Q-Yo</th>
<th>Q-n</th>
</tr>
</thead>
<tbody>
<tr>
<td>P#3-3</td>
<td>1.00</td>
<td>0.19</td>
<td>-0.33</td>
<td>0.46</td>
</tr>
<tr>
<td>$R_{\text{sol}}$</td>
<td>1.00</td>
<td>0.19</td>
<td>-0.33</td>
<td>0.46</td>
</tr>
<tr>
<td>$R_{\text{ct}}$</td>
<td>0.19</td>
<td>1.00</td>
<td>-0.52</td>
<td>0.49</td>
</tr>
<tr>
<td>Q-Yo</td>
<td>-0.33</td>
<td>-0.52</td>
<td>1.00</td>
<td>-0.89</td>
</tr>
<tr>
<td>Q-n</td>
<td>0.46</td>
<td>0.49</td>
<td>-0.89</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Figure 5.14 Nyquist and Bode plots of impedance spectra measured in solution 0.5M H$_2$SO$_4$, 0.005M Fe$_2$(SO$_4$)$_3$ and 0.005M Fe(SO$_4$) at 420 mV vs. SCE using a microelectrode technique with fit curves according to model $R_{sol}(R_{ct}Q)(R_{ss}C_{sc})$ shown for three different electrodes (P#1-2 top, P#1-3 middle and P#1-4 bottom).
Figure 5.15 Nyquist and Bode plots of impedance spectra measured in solution 0.5M H₂SO₄, 0.005M Fe₂(SO₄)₃ and 0.005M Fe(SO₄) at 420 mV vs. SCE using a microelectrode technique with fit curves according to model $R_{sol}(R_{ct}Q)$ shown for three different electrodes (P#2-1 top, P#2-2 middle and P#1-3 bottom).
Figure 5.16 Nyquist and Bode plots of impedance spectra measured in solution 0.5M \( \text{H}_2\text{SO}_4 \), 0.005M \( \text{Fe}_2(\text{SO}_4)_3 \) and 0.005M Fe(SO\(_4\)) at 420 mV vs. SCE using a microelectrode technique with fit curves according to model \( R_{\text{sol}}(R_{\text{ct}}Q) \) shown for three different electrodes (P#3-1 top, P#3-2 middle and P#3-4 bottom).
Figure 5.17 Nyquist and Bode plots of impedance spectra measured in solution 0.5M H$_2$SO$_4$, 0.005M Fe$_2$(SO$_4$)$_3$ and 0.005M Fe(SO$_4$) at 420 mV vs. SCE using a microelectrode technique with fit curves according to model $R_{sol}(R_{ct}Q)$ shown for three different electrodes (P#4-1 top, P#4-2 middle and P#4-3 bottom).
Statistical analysis procedures were applied to fit the data and estimate parameters of the equivalent circuit, which the average of these estimates is presented in Table 5.15.

The parameters of the equivalent circuit providing the best fit were obtained by minimizing the value of $\chi^2$, which is expressed as follows:

$$
\chi^2 = \sum_{k=1}^{n} \left[ W_{Re}(Z_{k,Re,cal} - Z_{k,Re,meas})^2 + W_{Im}(Z_{k,Im,cal} - Z_{k,Im,meas})^2 \right]
$$

where

- $W_{Re}$ = weighting factor for real part ($\Omega^{-2}$)
- $W_{Im}$ = weighting factor for imaginary part ($\Omega^{-2}$)
- $n$ = number of data points (-)
- $Z_{k,Re,cal}$ = calculated real impedance at point k ($\Omega$)
- $Z_{k,Im,cal}$ = calculated imaginary impedance at point k ($\Omega$)

$W_{Re}$ and $W_{Im}$ are used to obtain the same weight for the real and imaginary parts. The calculated $\chi^2$ values range from $2.2 \times 10^{-3}$ to $5.4 \times 10^{-3}$. These numbers show a very good agreement between experimental and the calculated results obtained from the best fitting equivalent circuit model.

Different circuit elements shown in Figure 5.5 used for modeling the frequency response of electrodes showed a range of values. This can be due to the non-uniform distribution of impurity elements acting as doping elements in different pyrite samples. In addition, some pyrite electrode surfaces may have favored a certain crystallographic axis that is more reactive. The impact of surface roughness on the values of measured circuit elements must also be considered.

In order to be able to cover a wide range of estimated values, the values of equivalent circuit elements are presented in plots showing mean values with their confidence intervals Figure 5.18.
Table 5.15  Average values of elements of equivalent circuit $R_{sol}(R_{ct}Q)(R_{ss}C_{sc})$ shown in Figure 5.5 based on 10 samples for each pyrite type.

<table>
<thead>
<tr>
<th>Pyrite type</th>
<th>$R_{sol}$ ($\Omega \text{cm}^2$)</th>
<th>$R_{ct}$ ($\Omega \text{cm}^2$)</th>
<th>$Q-Y_o$ ($\Omega \text{s}^{-n}$)</th>
<th>$Q-n$</th>
<th>$C_{sc}$ ($\text{F cm}^{-2}$)</th>
<th>$R_{ss}$ ($\Omega \text{cm}^2$)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>12.4</td>
<td>0.76×10$^3$</td>
<td>3.4×10$^{-4}$</td>
<td>0.66</td>
<td>4.8×10$^{-3}$</td>
<td>0.74×10$^3$</td>
<td>3.51×10$^{-3}$</td>
</tr>
<tr>
<td>#2</td>
<td>15.1</td>
<td>14.54×10$^3$</td>
<td>1.1×10$^{-4}$</td>
<td>0.70</td>
<td>-</td>
<td>-</td>
<td>4.31×10$^{-3}$</td>
</tr>
<tr>
<td>#3</td>
<td>10.6</td>
<td>15.33×10$^3$</td>
<td>1.4×10$^{-4}$</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
<td>2.22×10$^{-3}$</td>
</tr>
<tr>
<td>#4</td>
<td>9.6</td>
<td>16.27×10$^3$</td>
<td>0.9×10$^{-4}$</td>
<td>0.72</td>
<td>-</td>
<td>-</td>
<td>5.46×10$^{-3}$</td>
</tr>
</tbody>
</table>

5.3.2 Equivalent Circuit Element

5.3.2.1 Uncompensated Resistance

Although the potentiostat compensates for the solution resistance between the counter and reference electrodes, in a three-electrode cell even in this arrangement, the entire voltage drop due to solution resistance ($iR_s$) term is not eliminated from the measurements. Even using a fine-tipped “Luggin-Haber” capillary, to position the tip of the reference electrode as closely as possible to the working electrode, still results in a fraction of $iR_s$ being included. Moreover, placing a reference electrode too close shields the solution current path at the working electrode surface and thus creates other problems. Such resistance is referred to as the uncompensated resistance. Parameters such as the size and shape of the cell, the location of the reference electrode, the shape of the working electrode, and the size and position of the counter electrode can affect uncompensated resistance. Uncompensated resistance can also arise from the inherent resistivity of pyrite or from the electrical lead connecting it to the electrochemical instrumentation. Microelectrodes demonstrate their superiority over conventional electrodes in two ways. First, they can be placed very close to the reference electrode, taking advantage of cell geometry adjustment. Second, they have very small surface area; typically a factor of at least a thousand times smaller than a conventional electrode. Hence, the currents on microelectrodes tend to be small, in the nA range or lower, while achieving high current density. This makes the voltage drop due to uncompensated resistances almost negligible (Bard and Faulkner, 2006; Myland and Oldham, 2000). The related calculated values denoted by $R_{sol}$ encompassed in
Figure 5.18 shows that the solution resistance is statistically equal in all the experiments.

5.3.2.2 Charge Transfer Resistance

Charge transfer resistance is the barrier through which the electron must pass across the electrode surface to the redox species or from the redox species to the electrode. The resistance is dependent on the reaction, the electrode surface, and the electrode overpotential. As the overpotential increases, the resistance decreases. At a very small overpotential, the relationship between the charge transfer resistance and the exchange current density can be deduced from the Butler-Volmer equation. Thus, charge-transfer resistance ($R_{ct}$) can be defined as (Bard and Faulkner, 2006; Yuan et al., 2010):

$$R_{ct} = \frac{RT}{n_\alpha F i_0}$$

(5.2)

Charge transfer resistance can be used as an index of kinetic facility (Bard and Faulkner, 2006).

The variation in the measured values of charge transfer resistance is shown in Figure 5.18. To make inferences from the data, considering that the 95% confidence intervals shown for the mean values of pyrite #1 and the other three pyrites do not overlap, it can be concluded that the difference in charge transfer resistance of pyrite #1 compared to other pyrite types is statistically significant.

Now, comparing it to the batch leaching results shown in Figure 4.1, the statistical comparison proves that there is a significant positive correlation between those pyrite samples showing the best assisting effect on chalcopyrite batch leaching tests and the measured charge transfer resistance of different pyrite electrodes. The single most striking observation to emerge from the data comparison is that electrodes prepared from pyrite #1, showing the least charge transfer resistance, show the best assisting effect on the chalcopyrite batch leaching tests.
Figure 5.18  The mean values and error bar representation of equivalent analog circuit elements for four different pyrite samples. Error bars represent the 95% confidence interval for the mean value shown by diamonds, n=10.
In 2008, Lehner et al. demonstrated an existing difference in the values of measured charge transfer resistance in different synthetic pyrite electrodes. They also reported a contradiction between their findings when using the EIS method and AC voltammetry to investigate the effect of doping elements on the kinetic facility of different synthetic pyrite samples.

Interestingly, they found higher charge transfer resistance values for the electrodes with a higher AC voltammetry response. Since AC voltammetric measurement scans provide accurate information about fast interfacial charge-transfer kinetics, the magnitude of AC response can be considered as a measure of kinetic facility. So they were expecting a low charge transfer resistance to correlate with high AC response.

They explained this contradiction by considering that the EIS data are recorded over a longer time period, compared to the AC voltammetry scan, allowing a surface buildup of reaction product perhaps containing elemental sulfur. They concluded that electrodes with higher AC response would also be the ones to accumulate more reaction products resulting in higher charge transfer resistance.

The present findings seem to be consistent with the effect of different pyrite samples on leaching results presented in Figure 4.1 and the variable rate of ferric reduction current densities on the same pyrite samples shown in Figure 5.1, Figure 5.2 and Figure 5.3.

5.3.2.3 Constant Phase Element

The impedance response of the double-layer at a solid electrode is complicated by the fact that it does not show the ideal behavior as a pure capacitance (i.e., loss free, frequency independent) but rather shows a distribution of reactivity which is commonly categorized under distributed elements represented in equivalent electrical circuits as a constant phase element (CPE) (Brug et al., 1984; Orazem et al., 2008).

It has conclusively been shown by Brug et al. (Brug et al., 1984), that CPE for metal electrodes is due to the surface roughness and occurs as a result of surface coupling between the non-homogenous double layer capacitance and electrolyte resistance.
CPE, represented by \( Q \) is usually employed in a model in place of a capacitor to compensate for the non-homogeneity of the system (Figure 5.19). This non-homogeneity may be caused by the crystallographic irregularities on the surface leading to variations of the flat band potential and subsequently the space charge capacitance, or may be an effect of the nonhomogeneous surface doping elements (Ndzebet et al., 1994; van den Eeden et al., 1984).

To describe such a response, it is convenient to write the CPE admittance as:

\[
Y_{CPE} = Y_0(j\omega)^n
\]

(5.3)

Where \( \omega \) is the radial frequency, \( Y_0 \) is a factor of proportionality, and \( n \) with a value in the range of \(-1\) to \(1\) is the constant phase angle used to describe the non-ideal capacitance behavior of the metal/solution interface characterizing the phase shift. For integer values of \( n \) (\( n = 1, 0, -1 \)), the CPE characterizes \( C \) (capacitance), \( R \) (resistance), and \( L \) (inductance), respectively.

For \( n = 1 - \varepsilon \), a value of \( \varepsilon \) between 0 and 0.2 can correspond to distortion of the capacitance related to electrode surface roughness or distribution and accumulation of charge carriers. For \( n = 0.5 \pm \varepsilon \), a value of \( \varepsilon \) in the range of 0 and 0.1 can attribute the CPE to diffusion, with deviations from Fick's second law. For \( n = 0 \pm \varepsilon \), where \( \varepsilon \) ranges between 0 and 0.2, the CPE characterizes distorted resistance. Negative values of \( n \) for CPE are a sign of inductive energy accumulation (Yuan et al., 2010). Comparison of the value of \( n \) among different groups shows that the CPE behaves more like a capacitance with the mean value range of \( n \) ca. 0.66 to 0.75. No direct correlation was observed between the assisting effect of pyrite in chalcopyrite leaching and the values of \( n \), nor \( Y_0 \), among the different pyrite samples tested.

### 5.3.2.4 Warburg Impedance

At low frequencies, the Nyquist plots show a phenomenon of diffusion apparent by the presence of a diagonal line approximately 45° from the x-axis. The Warburg impedance is commonly associated with the diffusion process. At high frequencies the Warburg
Impedance is small because the diffusing reactants do not need to move very far. Warburg impedance is expressed by the following equation (Barsoukov et al., 2005):

\[ Z_W = \sigma \omega^{-1/2} - j \sigma \omega^{-1/2} \]  

(5.4)

where \( j \) is the imaginary number equal to \((-1)^{1/2}\) and constant \( \sigma \), called the Warburg coefficient, is related to the chemical diffusion of the electroactive species in electrode or electrolyte, and can be defined thus:

\[ \sigma = \frac{R T}{n^2 F^2 A \sqrt{2}} \left( \frac{1}{C_O D_O} + \frac{1}{C_R D_R} \right) \]  

(5.5)

where  
- \( D_O \) = diffusion coefficient of the oxidant (cm\(^2\)/s)  
- \( D_R \) = diffusion coefficient of the reductant (cm\(^2\)/s)  
- \( A \) = surface area of the electrode (cm\(^2\))  
- \( n \) = number of electrons involved (–)  
- \( C_O \) = concentration of the oxidant (M, mol/cm\(^3\))  
- \( C_R \) = concentration of the reductant (M, mol/cm\(^3\))  
- \( F \) = Faraday constant (C)  
- \( R \) = gas constant (J mol\(^{-1}\) K\(^{-1}\))  
- \( T \) = absolute temperature (K)

Whenever in an electrode process diffusion to a planar interface affects the kinetics of charge transfer or adsorption, Warburg impedance needs to be considered in the equivalent circuit. A high value of coefficient \( \sigma \) shows that the process is a diffusion rate-controlled process (Bard and Faulkner, 2006; Barsoukov et al., 2005).

The Warburg impedance might be associated with diffusion of ferric ions to the pyrite electrode/electrolyte interface. Thus, in two of the analog circuit models the Warburg impedance was used, but did not result in the best fit to the datasets not considerably improving the \( \chi^2 \) value. All the correlation matrices showed that the Warburg impedance is highly correlated to other elements in these models making it an extraneous element. Thus, in the proposed model in this study this element was not included.
Figure 5.19  Schematic relating the electric circuit elements to corresponding physical components based on Gerischer model of distribution of energy states (Gerischer, 1961 and 1970).

5.3.2.5 Capacitance

Capacity measurement indicates a measure of the charge storage during half an AC cycle, with the charge returned during the other half of the cycle. At the surface of a semiconductor electrode, several contributions to the capacity, corresponding to various places where charge is stored, can be identified. These capacitances can be across the Helmholtz layer, across the semiconductor space charge region, in surface states, and across an oxide film at the surface. Among the above mentioned capacitances in the analog equivalent circuit, the pyrite/solution interface is modeled using space charge capacitance and the double layer (Helmholtz) capacitance.

In pyrite#1 due to its lower charge transfer resistance, the space charge capacitance which is a characteristic of a semiconductor is measured. In pyrite types #2, #3 and #4, in the employed range of frequencies, other possible elements of the equivalent circuit
including surface charge capacitance were not estimated. This is mainly caused by high charge transfer resistance of these pyrite samples overshadowing other circuit elements and instrumental limitations in lower frequencies.

5.3.2.6 Surface State Resistance

Semiconductors are modeled with band theory where a forbidden region (band gap) separates the valence and conduction bands. At the semiconductor-electrolyte interface, the abrupt termination of a crystal lattice generates discrete energy levels within the band gap called surface states, which are physically and chemically different from within the bulk. Surface states may arise from the dangling bonds of unfilled valences on surface atoms, defects in the crystal structure, formation of oxide layers, or adsorbed chemical species. Surface states complicate the quantitative investigation of semiconductor electrodes by mediating charge transfer, trapping and releasing charge carriers, providing recombination centers, and allowing applied potential drops to occur at the surface rather than the space charge region. The presence of these electrically active surface states leads to an additional interfacial impedance which relies on the specific processes taking place (Koval and Howard, 1992).

Since transfer of electrons from a semiconductor to an electrolyte is dependent on the relative energy levels of the charge carriers in the semiconductor and the electrolyte, different pyrite samples show different responses. The electron transfer can occur when the orbital energy of the accepting ions in the solution is the same or lower than the energy of the electrons in the semiconductor. The presence of surface states causes the redox couple in the solution to stay in a favorable energy position with respect to the band gap. Therefore, the existence of a large number of surface states within the band gap causes the pyrite to exhibit metallic behavior, and a different response to the electrochemical measurements is the result. In such a case, the Fermi level is pinned to the energy levels of the solution redox couple (Bard and Faulkner, 2006; Morrison, 1980).

In the absence of excess minority carriers (holes in n-type pyrite), the surface states are generally supposed to interact with the conduction band. In this case, conduction-band
electrons are reversibly trapped and released at the surface states according to the following equation:

\[ SS^0 + e^-(CB) = SS^- \]  \hspace{1cm} (R5.1)

In the presence of a Fe\(^{3+}/Fe^{2+}\) redox couple in solution, it is also possible for charge transfer to occur between the surface states and solution as follows:

\[ SS^- + Fe^{3+} = SS_0 + Fe^{2+} \]  \hspace{1cm} (R5.2)

\[ SS^0 + Fe^{2+} = SS^- + Fe^{3+} \]  \hspace{1cm} (R5.3)

Illumination generates holes in the valence band, giving rise to possible recombination via surface states represented by reaction (R5.1) for the electron capture step and reaction (R5.4) for hole capture and release:

\[ SS^- + h^+(VB) = SS^0 \]  \hspace{1cm} (R5.4)

Charge transfer processes occurring at surface states on semiconductor electrolyte interfaces can be categorized under four main models: Case 1: Shallow surface states in the dark that only interact with conduction bands (reaction (R.5.1)); Case 2: Shallow surface states that interact with the conduction band and with a redox couple in solution (reactions (R5.1), (R5.2) and (R5.3)); Case 3: Surface recombination centers that capture holes from the valence band and electrons from the conduction band (reactions (R5.1) and (R5.4)); and Case 4: Surface states that are located close enough to the conduction band that they can interact with it, and thereby act as recombination centers (reactions (R5.1) and (R5.4)). For more detailed explanations and further discussion of diagnostic parameters, readers are referred to the work of Hoffman et al. (1998).

For pyrite types #2, #3 and #4 due to the large value of charge transfer resistance the estimation of surface state resistance was not successful. Surface state resistance for pyrite #1 showed a small value ruling it out as rate determining step in the kinetics (Table 5.15).

Other circuit elements such as recombination resistance and capacitance can also be placed in the equivalent circuit as an inner loop circuit as done by Lehner et al. (2008).
While this might give a better fit to the data set, these values do not display a clear trend and thus may not be physically meaningful. No third time constant and in some cases not even a second time constant is observed in our data, these other elements might be detectable in lower frequencies, however due to instrumental limitations low frequency data was highly noisy and no meaningful information could be extracted.

5.4 Kramers-Kronig Validation of the Impedance Data

Employing low amplitude excitations and existing inherent noise makes data validation in EIS a necessity. Kramers-Kronig relations are often used to ascertain the validity of EIS data. They are used to check whether experimental data display the characteristics of a linear, causal, and stable system imposed by linear systems analysis. Kramers-Kronig transforms are pure mathematical integral relations, connecting the real part and imaginary part of the impedance deduced from Cauchy's theorem of complex variable functions. In their most common form, as used in electrochemistry, the transforms are written as follows (Macdonald and Urquidi-Macdonald, 1985):

$$Z_{Re}(\omega) = Z_{Re}(\infty) + \frac{2}{\pi} \int_0^\infty \frac{xZ_{Im}(x) - \omega Z_{Im}(\omega)}{x^2 - \omega^2} dx$$  \hspace{1cm} (5.6)

$$Z_{Im}(\omega) = -\frac{2\omega}{\pi} \int_0^\infty \frac{Z_{Re}(x) - Z_{Re}(\omega)}{x^2 - \omega^2} dx$$  \hspace{1cm} (5.7)

Where \(\omega\) is the frequency of transform and \(x\) is the frequency of integration. Since the measured frequency range is typically insufficient to allow integration over the frequency limits of zero to infinity, different approaches have been proposed by researchers to circumvent this problem (Agarwal et al., 1992; Esteban and Orazem, 1991; Kendig and Mansfeld, 1983; Macdonald and Urquidi-Macdonald, 1985; Orazem et al., 1991).

In this study the approach described by Esteban and Orazem (1991) was used. This approach is different from other algorithms in that it does not use polynomials or the \textit{a priori} assumption of a model to extrapolate data below the lowest measured frequency. In this approach, Esteban and Orazem (1991) proposed that, rather than predicting the imaginary impedance from the measured real impedance using equation (5.7) or, alternatively, predicting the real impedance from the measured imaginary values using
equation (5.8), both equations (5.7) and (5.8) could be applied together and simultaneously to calculate the impedance values below the lowest measured frequency. A low-frequency limit, which is three or four orders of magnitude smaller than the lowest measured frequency, can be chosen for integration of the Kramers-Kronig transforms (Agarwal et al., 1995a).

The calculated impedance, in the frequency range between the lowest measured frequency and the low-frequency limit, forced the experimental data points to satisfy the Kramers-Kronig relations in the frequency range between the maximum measured frequency and the low-frequency limit (Esteban and Orazem, 1991).

Chi-squared ($\chi^2$) values in the range of $10^{-3}$ were obtained in all cases. Figure 5.20 shows the percentage error between the recalculated data set after applying the Kramer-Kronig relations and the measured data over the whole frequency domain. The calculated value of the chi-squared ($\chi^2$) in this case is $1.28\times10^{-3}$ and the percentage error is less than 6%.
Figure 5.20  Relative residual error percentage between the equivalent circuit fit $R (RQ)(CR)$ after applying the Kramer-Kronig relations and the data set over the whole frequency domain.

While the algorithm explained here has been applied to my experimental data with success, it is worth noting that any approach toward extrapolation of data can be applied only over a small frequency domain. In cases where frequency domain is so small that the data do not show a maximum in the imaginary impedance, this algorithm cannot be used. Measurement models introduced by Agarwal et al. (1992) can be used as a superior tool to identify the frequency-dependent error structure of impedance data and to check the consistency of the data with the Kramers-Kronig relations. In the measurement-model approach, experimental data can be checked for consistency with the Kramers-Kronig relations without explicit integration of the Kramers-Kronig relations; thus, inaccuracies caused by extrapolation of an incomplete frequency domain are circumvented (Agarwal et al., 1992; Agarwal et al., 1995 a and b).
5.5 Mott-Schottky Study

The classical work of Dewald (1960) on single crystal ZnO-electrolyte interfaces and the excellent agreement between his experimental results and Mott-Schottky theory validated a new pathway for analyzing semiconductor-electrolyte interfaces. His work provided a new method for a deeper investigation of the structure of the semiconductor-electrolyte interface to electrochemists. In this study the microelectrode technique with Mott-Schottky analysis was applied to investigate the differences between single particles of different pyrite samples.

In order to characterize the semiconducting properties of pyrite, Mott-Schottky plots were acquired. Mott-Schottky is a plot of $C_{SC}^{-2}$ vs. semiconductor electrode potential $V$, which yields a straight line from which the flat-band potential $V_{fb}$ can be found from the intercept on the $V$ axis.

When potential is applied to a semiconductor-electrolyte interface, two capacitances should be considered in series: the double layer (Helmholtz) capacitance and the space charge region capacitance. For a moderately concentrated electrolyte, generally the Helmholtz capacitance on the electrolyte side of the interface is assumed to be much larger (by 2 or 3 orders of magnitude) than the space charge capacitance. Therefore, total potential drop can be taken across $C_{SC}$ only, and the measured capacitance value will be equal to the space charge capacitance given by the Mott-Schottky equation (Bard and Faulkner, 2006; Memming, 2001; Morrison, 1980):

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon_0 \epsilon A N_D} \left( V - V_{fb} - \frac{kT}{e} \right)$$

where

- $C_{SC}$ = space charge capacitance (F)
- $e$ = elementary charge, $1.602 \times 10^{-19}$ (C)
- $\epsilon$ = relative dielectric constant of the semiconductor (–)
- $\epsilon_0$ = permittivity of free space, $8.854 \times 10^{-12}$ (F/m)
- $A$ = surface area of the electrode (m$^2$)
- $N_D$ = donor density (cm$^{-3}$)
- $V$ = applied potential (V)
$V_{fb}$ = flat band potential (V)

$k$ = Boltzmann constant, $8.617 \times 10^{-5}$ (eV/K)

$T$ = absolute temperature (K)

The value for relative dielectric constant of pyrite equals $10.9 \pm 0.5$ (Husk and Seehra, 1978). For $p$-type semiconductors acceptor density ($N_A$) is used.

There are several factors leading to deviations from ideal Mott-Schottky behavior. For simple Mott-Schottky behavior, in the derivation of the Mott-Schottky equation and the definition of the parameters involved, a set of assumptions are made as follows: (1) the resistance of the electrolyte and the bulk semiconductor are zero; (2) finite resistance in parallel to the barrier capacitance is absent; i.e., the barrier has ideal blocking properties; (3) surface states effects are absent; (4) the relative dielectric constant of the semiconductor is frequency-independent; (5) only one type of completely ionized donor or acceptor is present; (6) electronic defects are distributed uniformly; and (7) the semiconductor-electrolyte interface is perfectly planar and two-dimensionally infinite (Cardon and Gomes, 1978).

The value of $N_D$ can also be conveniently calculated from the slope knowing the values of $\varepsilon$ and $A$ for a specific electrode using equation below (Memming, 2001; Morrison, 1980; Mott, 1939; Schottky, 1939; Schottky, 1942b).

$$N_D = \frac{2}{(\varepsilon \varepsilon_0 \times \text{slope})}$$

(5.9)

Schieck et al. (1990) performed Hall measurements using the van der Pauw method and reported values ranging from $6.9 \times 10^{15}$ to $5.4 \times 10^{17}$ cm$^{-3}$ for doping density for both natural and synthetic pyrite samples of $n$-type and $p$-type. Ferrer et al. (2003) reported measured values from $2 \times 10^{18}$ to $10^{22}$ cm$^{-3}$ in doped $p$-type pyrite films and from $6 \times 10^{17}$ to $10^{21}$ cm$^{-3}$ in doped $n$-type pyrite films. Bueker et al. (1992) obtained $2 \times 10^{16}$ cm$^{-3}$ for synthetic $n$-type pyrite crystals. Altermatt et al. (2002) concluded that the higher doping density in pyrite thin film is caused by crystal defects acting as dopants in pyrite.
The experimental Mott-Schottky plots for the four different pyrite samples are depicted in Figure 5.21. The pyrite electrode surface area in contact with the electrolyte was considered in the calculations.
Figure 5.21 Mott-Schottky plots for pyrite electrodes prepared from pyrite samples #1 to #4 using a microelectrode. Error bars are showing standard deviations for 10 samples (solution: 0.5M H₂SO₄, 0.005M FeSO₄ and 0.005M Fe₂SO₄).
By measuring the flat band potential; i.e., the bias which would make the band bending zero, the position of the Fermi level, $E_F$, can be determined with respect to SCE. Knowing $V_{fb}$ for pyrite is essential for the construction of an energy model for the pyrite-electrolyte interface. With this value, comparison of various semiconductors, with each other as well as with the energy levels of chemical species existing in solution, becomes possible (Lemasson et al., 1981).

Effective density of states at the bottom of the conduction band $N_C$ is calculated as follows:

$$N_C = \frac{2}{h^3} (2\pi m_e^* kT)^{3/2} \quad (5.10)$$

where $N_C =$ effective density states at the bottom of the conduction band (cm$^{-3}$), $m_e^* =$ effective mass of the electron (kg), $h =$ Planck constant (J s), $k =$ Boltzmann constant (J/K), $T =$ absolute temperature (K).

Replacing the Fermi function with a simple exponential function, i.e., the Maxwell-Boltzmann distribution function for a nondegenerate semiconductor in the general carrier density equation results in equation (5.11). A nondegenerate semiconductor is defined when the Fermi energy is deep in the band gap, more than $2kT$ below the conduction band or more than $2kT$ above the valence band (Gerischer, 1961; Morrison, 1980). Banerjee et al. (1990) reported temperature variations in the electrical conductivity of natural pyrite crystals as an indication of the material being a nondegenerate semiconductor. Gadgil (1990) found pyrite to behave only as a degenerate semiconductor at temperatures higher than 530°C or when in sulfur-deficient form ($\text{FeS}_{2-x}$). In equation (5.11), $m_e^*$ is the effective mass of the electron. Dasbach (1994) obtained from experiments with Schottky diodes a value of $m_e^* = 0.25m_e$ for pyrite thin films in which $m_e$ is the mass of the electron in the free electron gas model. The value reported by Dasbach (1994) is in agreement with the value $m_e^* = 0.35m_e$ calculated by Zhao et al. (1993) using the energy-momentum band structure of pyrite. Kou and Seehra (1978) studied pyrite with optical absorption methods and
reported $m_e^* = 0.45m_e$. In the calculation the value reported by Kou and Seehra (1978) was used since they used natural pyrite crystals in their experiments.

Equation (5.11) can only be applied when the energy-momentum relation of the conduction band is parabolic in the range where it is occupied with electrons (Altermatt et al., 2002). According to Zhao et al. (1993) this is a valid presumption for pyrite.

Dasbach (1994) reported that for pyrite, the effective density of states $N_C = 3 \times 10^{18} \text{ cm}^{-3}$. Altermatt et al. (2002) found this number consistent with the measured net doping density as a function of temperature (Arrhenius plot), and in agreement with the work done by Bither et al. (1968) and Karguppikar and Vedeshwar (1988). Bueker et al. (1992) used a value of $N_C = 7.5 \times 10^{18} \text{ cm}^{-3}$ in their calculations.

The classical Maxwell-Boltzmann distribution corresponding to the flat-band situation may be written thus:

$$E_c - E_{F,b} = kT \ln \left( \frac{N_C}{N_D} \right)$$

(5.11)

where

$$E_{F,b} = -eV_{fb}$$

(5.12)

Therefore, by knowing the values of $N_D$, $N_C$ and $V_{fb}$, the energy band position $E_c$ can be determined. Consequently, the valence band edge energy ($E_v$) is calculated using the calculated values of conduction band edge energy ($E_c$) and experimentally measured values of the energy gap of pyrite ($E_g$) through optical characterization of pyrite, and using the following equation (Morrison, 1980; Nozik and Memming, 1996):

$$E_c - E_v = E_g$$

(5.13)

Since this Mott-Schottky plot is a straight line and its slope is identical to the theoretical value given by equation (5.9), it is suggested that the potential across the Helmholtz layer does not change with the applied bias. Therefore, any variation in electrode potential occurs only across the space charge layer. Consequently the energy band positions of $E_c$ or $E_v$ tend to be fixed with respect to the Fermi level (Nozik and Memming, 1996).
Dasbach (1994) mentions the value of band gap energy in the range of 0.9 to 0.95 eV for crystalline pyrite and 0.8 eV for thin films measured by quantum efficiency and the transmission reflection method. Kou and Seehra (1978) performed optical absorption studies in thin film natural single crystals of pyrite and reported a band gap energy range of 0.7 to 1 eV. In the calculation, the experimental value of 0.95 eV mentioned by Ennaoui et al. (1985 and 1986) was used.

Depending on geological conditions, natural pyrite can have a wide range of chemical compositions leading to slight differences in the measured values of band gap energies.

Figure 5.22 schematizes the energetic equilibrium band positions for $n$-type pyrite in contact with aqueous electrolyte deduced from the present results. For ease of drawing, the Fermi distribution is shown with a straight line instead of the actual curved shape.

![Energy band diagram](image)

**Figure 5.22** Schematic energy band positions on SCE scale for the $n$-type pyrite/solution interface.

The flat band potential $V_{fb}$ and, consequently, the position of the energy bands can change with the pH of the solution because of protonation and deprotonation on the electrode surface. Therefore, the energy bands remain fixed at a constant pH.
The built in voltage or the band bending $V_{bi}$ is generally taken as the difference between the Fermi level of the electrolyte, which is taken as the redox potential of the electrolyte $V_{F,\text{redox}}$. For the Fe$^{3+}$/Fe$^{2+}$ couple the potential was measured at 415 mV vs. SCE. The parameter $V_{bi}$ is called the built in voltage because it is built in to the semiconductor as a result of equilibration with the solution redox level (Tan et al., 1994):

$$V_{bi} = V_{F,\text{redox}} - V_{fb}$$  \hspace{1cm} (5.14)

The barrier height $\Phi_b$, which depends only on the initial position of the semiconductor conduction band edge and the initial electrochemical potential of the electrolyte at the electrode surface, is calculated as follows (Tan et al., 1994):

$$\Phi_b = V_{bi} + \frac{(E_c - E_F)}{e}$$  \hspace{1cm} (5.15)

The depletion width $W$ is calculated as follows (Tan et al., 1994):

$$W = \left(\frac{2e\epsilon\epsilon_0 V_{bi}}{eN_D}\right)^{\frac{1}{2}}$$  \hspace{1cm} (5.16)

The ideal simplified electrostatic theory defines a blocking semiconductor-electrolyte interface as a perfect capacitor. Some experimental results show that the capacitance of a semiconductor-electrolyte interface can depend on the measuring frequency. This so called frequency dispersion can lead to unreliable calculated values of both the slope and the extrapolation of $C^{-2}$ vs. $V$ in the Mott-Schottky plot. In order to verify that the parameters obtained from the plots are independent of the frequency employed in the capacitance measurements, the measurements were carried out over a broad frequency range. Figure 5.21 also compares the results obtained at 10 kHz and 20 kHz. No significant differences were found between the measured data at different frequencies (Bard and Faulkner, 2006; Hens and Gomes, 1999a; Hens and Gomes, 1999b). Nozik (1978) mentions a series of extensive studies attempted on the frequency dependence of Mott-Schottky plots and attributed it to the presence of surface irregularities and/or surface states in the semiconductor. The frequency dependent data was categorized into two classes. In the first class, the Mott-Schottky plots at different frequencies are parallel to each other, which results in a different $V_{fb}$ for
each frequency. In the second class, the Mott-Schottky plots have different slopes but converge to a common intercept, resulting in a common $V_{fb}$.

Using these plots and equations (5.9) to (5.17), various parameters of pyrite as a semiconductor as well as the pyrite-electrolyte interface were calculated, which are shown in Table 5.16. In the development of this table, it was assumed that, for a moderate value of donor density ($N_D < 10^{18} \text{ C m}^{-3}$) in contact with a moderately concentrated electrolyte, the inequality $C_{SC} << C_H$ is generally satisfied under depletion conditions. Therefore, it was expected that the blocking semiconductor-electrolyte interface would constitute a perfect capacitor, the capacitance $C$ of which depends on the applied potential $V$ according to equation (5.9).

From the data presented in Table 5.16 it can be seen that the parameters for different pyrite samples are qualitatively similar. However, the following points of difference in the measured values, although not considerable in some cases, are of interest:

- The value of flat band potential $V_{fb}$ is the largest for pyrite #1 and decreases to pyrite #4. Consequently, the value of built in voltage $V_{bi}$ increases accordingly. This parameter is important from the photoelectrochemical point of view since the maximum electrochemical solar cell voltage obtainable for any electrolyte is equal to $V_{bi}$.
- The value of the donor density ($N_D$), is the largest in pyrite #1 and decreases to pyrite #4.
- The value of depletion layer width $W$ is the lowest in pyrite #1 and increases from pyrite #1 to pyrite #4.
- In pyrite #4, which has fewer impurities, the standard deviations of measured data points is less, compared to other pyrite electrodes.

This means that in pyrite #4 the charge has to come toward the surface from deeper within the bulk of the pyrite in order to obtain the proper number of ionizable charges from the solid to equilibrate with electrolyte $V_{F, \text{redox}}$. In other words, for pyrite #1, the situation of electrostatics at the pyrite-electrolyte becomes more akin to metal-
A larger depletion width means a higher quantum yield, a parameter of considerable interest to photoelectrochemists.

In the Mott-Schottky plot in Figure 5.21, two relatively well defined linear portions with both positive and negative slopes can be seen. The difference in slopes of the Mott-Schottky plot reveals a difference in electronic behavior of the outer surface layers of the electrode, which are near the electrolyte. In the case of Figure 5.21, for potentials approximately less than 600 mV, the plot has a positive slope, which indicates that pyrite is $n$-type. At higher potentials, the slope changes to negative, indicating that the electrode surface has changed to $p$-type. Minor slope changes due to a change of the electrical properties of the surface of the pyrite electrode would have been noticeable at different potentials in both sections of the curves, had the data points not been presented by their mean values.

Referring back to Figure 5.1 and Figure 5.2, it is observed that during the initial anodic scan, the current was very low until the potential reached about 0.65 V, after which there was a sharp rise in current (peak A1). During oxidation of pyrite, iron-deficient pyrite, sulfate and polysulfides form. Small, time-dependent currents observed at potentials below 0.65 V on the first scan suggest that such a surface layer inhibits oxidation. According to Doyle and Mirza (1996), a $p$-type semiconducting layer formed on the surface generates a $p$-$n$ junction with underlying pyrite that is reverse biased for passing an anodic current. However, they did not present any experimental evidence to support this claim. Here in Figure 5.21 the transition from $n$-type to $p$-type on the surface of pyrite electrode is clearly shown.

The break in the Mott-Schottky plot occurs around 0.65 V. This break as seen in the voltammogram is very close to the potential at which reaction (R4.11) occurs. As a result, it is suggested that the formation of the reaction products of reaction (R4.11) on the surface changes the electrical properties of the surface in this potential region.

Finally, these results must be interpreted with caution because of the small sample size used in this study. Findings may not be transferable to all pyrite samples due to the
vast variation in the compositional, trace element, textural and electrical properties found in pyrites from different sources.
Table 5.16  Summary of the results obtained from the Mott-Schottky plots of four different pyrite samples.

<table>
<thead>
<tr>
<th></th>
<th>Pyrite #1</th>
<th></th>
<th>Pyrite #2</th>
<th></th>
<th>Pyrite #3</th>
<th></th>
<th>Pyrite #4</th>
<th></th>
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<td>4.3</td>
<td>4.5</td>
<td>4.8</td>
<td>5.1</td>
</tr>
<tr>
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CHAPTER 6: Raman Spectroscopy of Chalcopyrite and Pyrite

Far too little attention has been paid to the sulfur species that form during Galavox™ leaching process on the surface of pyrite and chalcopyrite. One of the hypotheses for the inconsistent catalytic behavior of pyrite was the possibility of formation of various sulfur species on various pyrite samples.

Micro Raman spectroscopy was employed to characterize the surface species produced during leaching on both chalcopyrite and pyrite and thereby to determine the phenomena that occur.

To demonstrate the reproducibility of spectra, multiple measurements were taken from each sample. One representative spectrum was selected and displayed herein. Several spectra contained relatively high noise to signal ratios, to the point where small peaks were indistinguishable from the background. These were omitted. However, orientation of the crystal lattice, optical properties of the crystal, presence of local impurities, and irregularities in the crystal structure may cause the band positions and relative band intensities reported here to be marginally distorted, and thus possibly to vary slightly from those reported previously in the literature.

6.1 Raman Spectra of Sulfur

Cyclooctasulfur ($\alpha$-S$_8$) has a face-centered, orthorhombic crystal structure and is the stable STP form of sulfur (Cotton et al., 1998; Meyer, 1976). Group theory predicts 48 Raman active and 33 infrared active bands for vibrations within the unit cell. However, many of these 48 Raman active modes are either too weak to be observed or too close to other bands that they cause an overlap (Anderson and Loh, 1969; Palik et al., 1998).

The Raman spectrum was recorded on pure sublimed flowers of elemental sulfur (Fisher Scientific) which predominantly contain $\alpha$-S$_8$. The typical impurities present in sulfur flowers are other allotropes of sulfur consisting of trivial amounts of polymeric insoluble sulfur (S$_\mu$) and trace amounts of S$_7$ along with organic impurities (Steudel and
In the production process, the polymer forms from reactive small sulfur molecules present in sulfur vapor, which are unstable at ambient temperatures and react to a mixture of $S_8$ and $S_\mu$ on quenching (Steudel and Eckert, 2003).

Figure 6.1 depicts the Raman spectrum of $\alpha$-$S_8$ in the 100–500 cm$^{-1}$ range. The most dominant band is recorded at 470 cm$^{-1}$ due to S–S stretching vibrations and is assigned as $\nu_1$. The two bands at 150 and 210 cm$^{-1}$ arise from the bending of the S–S–S chain assigned as $\nu_8$ and $\nu_2$. Some other bands of lower intensity are also observed in the spectra of sulfur, which are due to overtones and combinations of the stretching and bending modes. The presented spectra appear to be generally consistent with the previously published investigations of the Raman spectroscopy of sulfur (Anderson and Loh, 1969; Eckert and Steudel, 2003; Harvey and Butler, 1986; Li et al., 1993).
Figure 6.1 Raman spectra obtained from a) S$_8$ b) chalcopyrite, and c) pyrite.
6.2 Raman Spectra of Chalcopyrite

The acquired spectrum of a fresh chalcopyrite sample is depicted in Figure 6.1 b. Due to the overlap of Raman active bands and low scattering intensity of this material, it is hard to acquire distinctive, well-resolved peaks except that of the A\textsubscript{1} symmetry mode. Therefore, chalcopyrite spectra are characterized by a prominent band arising from the interaction of incident radiation with the A\textsubscript{1} symmetry zone center phonon. This main band occurs at 293 cm\textsuperscript{-1}. There are two weaker bands visible at 320 and 353 cm\textsuperscript{-1} which are attributed to the either B\textsubscript{2} or E modes (Izquierdo-Roca \textit{et al.}, 2011; Mernagh and Trudu, 1993; Parker \textit{et al.}, 2008b; Rincón \textit{et al.}, 1999). For further details on the symmetry of modes readers are referred to the book by Hargiatti and Hargiatti (1995). There is also high background noise in this region indicating an overlap of bands at similar frequencies. The obtained spectrum of chalcopyrite Raman bands displays good agreement with those observed by previous researchers (Izquierdo-Roca \textit{et al.}, 2011; Mernagh and Trudu, 1993; Parker \textit{et al.}, 2008b; Rincón \textit{et al.}, 1999).

The quality of obtained spectra on leached chalcopyrite samples was not satisfactory. In chalcopyrite leached in the presence of pyrite #1, the sulfur layer was either dispersed in the solution or dissolved in the form of sulfate. On the particles with a layer of sulfur around them, the layer was too brittle due to porosity and was destroyed upon transfer to the microscope. The spectrum obtained from the chalcopyrite sample leached in the presence of pyrite #4 replicated those presented by Parker \textit{et al.} (2008a) on oxidized chalcopyrite that had been partially leached. As Parker \textit{et al.} (2008a) explain, the lack of success in obtaining a meaningful spectrum is based on the fact that standard Raman spectroscopy is not sufficiently sensitive to detect thin product layers formed on dissolving chalcopyrite. To solve this problem they employed Surface-Enhanced Raman Spectroscopy (SERS), which is a more sensitive technique. They showed that gold decoration enabled a surface-enhanced Raman effect to be usefully employed on the surface of oxidized chalcopyrite. One of the key challenges they faced in interpretation of their results was that the Raman-inactive product phase decomposed to polymeric sulfur under incident laser radiation. They did not detect any polysulfide species or sulfoxy anions. Similarly, I did not find standard Raman microscopy well
suited for studying the formed passive layer on the surface of chalcopyrite during leaching. Further studies taking advantage of SERS will need to be conducted.

6.3 Raman Spectra of Pyrite

Figure 6.1 c shows the Raman spectra acquired from a fresh pyrite sample featuring three bands. Lattice of pyrite resembles the NaCl structure, in which dumbbell-shaped disulfide ions ($S_2^{2-}$) occupy the chloride positions and iron atoms occupy the sodium positions. $S_2^{2-}$ ions lie at the center of the cube and at the mid-points of the cube edges. Each sulfur atom is coordinated with three iron atoms and one sulfur atom. Each iron atom is coordinated with six sulfur atoms in a tilted octahedral. Readers are referred to the papers published by Blanchard et al. (2005); Kleppe and Jephcoat (2004); Lutz and Willich (1974); Vogt et al. (1983) for detailed information on symmetry modes and Raman active modes of pyrite.

The first strong bands at $\sim 340 \text{ cm}^{-1}$ are due to S displacement perpendicular to the dumbbell ($S_2^{2-}$) bond axis ($E_g$). The second strong band at $\sim 380 \text{ cm}^{-1}$ is due to stretching vibration of dumbbell ($S_2^{2-}$) in phase throughout the crystal ($A_g$). There is also a weaker band observed at $\sim 430 \text{ cm}^{-1}$ due to a combination of various stretching and liberation modes or their combinations ($T_g$).

The shifts of the bands presented here corroborate the findings of other researchers (Lehmann et al., 2000; Li and Wadsworth, 1993; Parker and Hope, 2010; Sourisseau et al., 1991; Turcotte et al., 1993; Ushioda, 1972; Vogt et al., 1983). However, there are some slight differences in wavenumber values reported, especially in studies that have used single crystal pyrite samples.

Figure 6.2 presents the spectra acquired on the surface of pyrite #1 after different leaching times. By comparing them to the fingerprint spectra of some well-established sulfur allotropes such as $S_8$ (Figure 6.1 a) and $S_6$ (Eckert and Steudel, 2003; Nagata et al., 1992), and fresh pyrite (Figure 6.1 c), the bands have been categorized and labeled as P for pyrite and S for $S_8$. As can be seen in this figure, sulfur begins growing on the pyrite surface from the first sample which was after 4.5 hours. Raman scattering
measurements show that all the band intensities related to sulfur increased almost linearly with time after a rapid increase between 4.5 and 9 hours. No broad bands were observed between 440 and 470 cm\(^{-1}\) in these series of samples which would be associated with a sulfoxy anion or polysulfide.

Figure 6.2  Raman spectra of pyrite\#4 obtained from samples withdrawn during leaching.

The last sample (50 hours) shows that the sulfur bands acquired from pyrite completely match those of elemental sulfur (S\(_8\)). The comparison of the spectra shows that as leaching time passes, elemental sulfur becomes the predominant surface component. Longer leaching times appeared to give higher intensities of sulfur spectra.

Figure 6.3 shows the Raman spectra obtained from pyrite \#1 after different leaching times. In the spectra labeled as 1.5 hours, 3 hours and 4.5 hours, all three observed
bands match those of fresh pyrite. After 9 and 15 hours the pyrite bands remain, while four other bands also appear. Three of them, by comparison to Figure 6.1 a, have been assigned to the formation of elemental sulfur on the pyrite surface.

Figure 6.3 Raman spectra of pyrite#1 obtained from samples withdrawn during leaching.

The bands observed in the range of 440 and 460 cm$^{-1}$ in the spectra from the 9 and 15 hours samples of pyrite #1 shown in Figure 6.3, are considerably broader than those appearing in the spectrum obtained from $S_8$ (Figure 6.1 a). This range of broad bands observed on pyrite #1 is not characteristic of elemental sulfur. It seems possible that this broadness is due to the presence of polysulfides. A magnified version of these peaks is shown in Figure 6.4. While 30% of pyrite #1 particles displayed similar spectra to that shown in Figure 6.2, 70% displayed small peaks in the range of 440 and 460 cm$^{-1}$ as shown in Figure 6.3. In the studies conducted on the oxidation of pyrite by
Mycroft et al. (1990) and Li and Wadsworth (1993), similar bands were found in this wavelength region, which were attributed to polysulfides on the basis of previous Raman studies conducted by Janz et al. (Janz et al., 1976a; Janz et al., 1976b; Janz et al., 1976c) and El Jaroudi et al. (El Jaroudi et al., 1999a; El Jaroudi et al., 2000a; El Jaroudi et al., 1999b). The recorded Raman bands for S–S stretch frequencies of polysulfide species are as follows:

\[ S_3^{2-} \left( 458, 466, 472, \text{ and } 476 \text{ cm}^{-1} \right), \quad S_4^{2-} \left( 468, 478, 482 \text{ and } 485 \text{ cm}^{-1} \right), \quad S_5^{2-} \left( 479, 485 \text{ and } 488 \text{ cm}^{-1} \right) \text{ and } S_6^{2-} \left( 455 \text{ and } 495 \text{ cm}^{-1} \right). \]

Figure 6.4 A magnified version of the Raman spectra in Figure 6.3 for the 15 h sample.

Thermodynamic analysis of sulfur-based equilibria shows that forms of sulfur with intermediate valence states, including polysulfide ions and sulfoxyl anions, are
thermodynamically unstable (Bekturganov et al., 1997). In a Pourbaix diagram of sulfur species in aqueous solution, there are no regions of stability of these intermediate compounds. Therefore, metastable equilibria must be considered in the analysis of sulfur-containing systems. However, experiments have shown that polysulfide and sulfoxy anions are extremely stable, and can maintain their properties over long periods (Bekturganov et al., 1997).

Lehmann et al. (2000) interpreted this band (440–473 cm$^{-1}$) to be thiosulfate. Their reasoning is based on similar strong S–S stretching bands at 443 cm$^{-1}$ reported by other researchers (Gonnissen et al., 1998; Rintoul et al., 1997; Sato et al., 1985) for thiosulfate ions in solution.

The above interpretation presented by Lehmann et al. (2000) agrees with assertions that pyrite oxidation occurs via different multistage pathways. There is still significant conjecture in the literature as to the actual oxidation pathway of pyrite. This is largely because the processes of aqueous oxidation of pyrite involve a complex series of elementary reactions. During the oxidation of pyrite, sulfur must change oxidation state from $-1$ to $+6$ or transfer seven electrons through the semiconducting crystal to an oxidant in order to release iron (II) and sulfate ions to solution. According to Basolo and Pearson (1967), electron transfer reactions are limited to one or at most, two electrons. Ergo, this electronic transfer cannot occur in a single step (Moses et al., 1987; Rimstidt and Vaughan, 2003).

The fact that pyrite is a semiconductor and the reactions are electrochemical in nature makes this process even more complicated. The mobility of electrons in the mineral, which allows the various reactions to occur at different sites, also adds to this complexity. Moreover, the semiconducting properties of pyrite are largely dependent upon the precise chemical composition of the particular sample, often influenced by the region from which a particular sample is obtained. Small differences in stoichiometry and the impurity elements influence electrical properties and may in turn significantly affect the reactivity of pyrite (Rimstidt and Vaughan, 2003).
Intermediate sulfoxy anions (sulfite, $\text{SO}_3^{2-}$, thiosulfate, $\text{S}_2\text{O}_3^{2-}$, and polythionates, $\text{S}_n\text{O}_6^{2-}$, $n = 4, 5,$ and $6$) have been identified in the pyrite oxidation process (Moses et al., 1987). Luther (1987) proposed that thiosulfate plays a role as an initial soluble intermediate in the reaction.

Although most observations of thiosulfate and polythionates as a product of pyrite oxidation in solution have been reported in the circumneutral pH range (Goldhaber, 1983; Moses et al., 1987; Schippers et al., 1996), there are several studies reporting the existence of thiosulfate and polythionates on the surface of pyrite at a low pH (Moses et al., 1987; and Descostes et al., 2004). According to Moses et al. (1987) and Descostes et al. (2004), in acidic solutions under their experimental conditions, there is a lower chance of observation of thiosulfate and tetrathionate during experiments, since thiosulfate is oxidized to tetrathionate, and subsequently to sulfate.

As Druschel (2003), and Williamson and Rimstidt (1993) explain, in aqueous solutions containing ferric at low pH, thiosulfate reacts to form tetrathionate as follows:

$$4\text{S}_2\text{O}_3^{2-} + 4\text{Fe}^{3+} \rightarrow 2\text{FeS}_2\text{O}_3^{+} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{Fe}^{2+} \quad (\text{R6.1})$$

The kinetics of redox reactions requires that the oxidant and reductant form an activated complex to allow the transfer of electrons. According to Fukui’s approach (Fukui, 1970) this requires the Highest Occupied Molecular Orbital (HOMO) of the reductant and the Lowest Unoccupied Molecular Orbital (LUMO) of the oxidant to have matching symmetry and energy. The oxidation of thiosulfate by molecular oxygen does not proceed in homogeneous systems because of a symmetry mismatch between the HOMO and LUMO. Xu and Schoonen (1995) studied the catalytic effect of pyrite on thiosulfate oxidation in detail and showed that pyrite catalyzes the reaction by accepting electrons from thiosulfate in its conduction band and then donating them to oxygen. In other words, the pyrite particles behave as short-circuited electrochemical cells, which overcome the symmetry barrier between the so called “frontier orbitals” of the two reactants (Xu et al., 1996). In the absence of the catalytic effect of pyrite, thiosulfate decomposes via homogeneous disproportionation to produce sulfite ($\text{SO}_3^{2-}$) and elemental sulfur as follows (Xu and Schoonen, 1995):
\[8 \text{SO}_3^{2-} + H^+ \rightarrow S_8 + 7\text{SO}_3^{2-} + \text{HSO}_3^-\]  \hspace{1cm} (R6.2)

At low pH, when the supply of iron(III) is limited, reactions (R6.1) and (R6.2) start competing, which results in thiosulfate conversion to either tetrathionate, or elemental sulfur and sulfite (Williamson and Rimstidt, 1993). Whereas in the presence of excess \(\text{Fe}^{3+}\), thiosulfate oxidizes to tetrathionate completely, to the exclusion of elemental sulfur formation (Druschel 2003; Druschel and Borda, 2006).

Druschel (2003) measured slower oxidation kinetics of polythionates in acid pH solutions containing excess \(\text{Fe}^{3+}\) ions, compared to the formation of polythionates from thiosulfate. Thus, if pyrite oxidation progresses through a thiosulfate pathway, significant amounts of polythionates are expected.

Descostes et al. (2006) explain that the failure of some studies on pyrite oxidation in low pH to detect a significant amount of metastable sulfoxyl anions in solution is due to rapid electron transfer at low pH. Moreover, the incongruence of the reaction products observed in the study done by Descostes et al. (2004), among others, suggests that intermediate species can also be removed from the solution as precipitates or gases. Considering this, the lifetime of intermediate species, or their occurrence in solution, are still an area that remains poorly understood.

Borda et al. (2003) and Borda et al. (2004) applied vibrational spectroscopy methods including in situ flow-through attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, to study the formation and step-wise oxidation of sulfoxyl anions at the pyrite surface during oxidation, by ferric and molecular oxygen at low pH. They observed the presence of multiple surface-bound sulfoxyl anions at the pyrite surface during oxidation, although they were unable to assign the exact sulfur species detected. Rimstidt and Vaughan (2003) suggest that at low pH, the majority of the terminal \(\text{S}–\text{SO}_3\) groups hold a proton, so they have the stoichiometry, \(\text{S}–\text{SO}_3\text{H}\). This causes more electrons to be transferred to the \(\text{S}–\text{S}\) bond; from there they will be transferred toward the absorbed protons resulting in the terminal sulfur being positively charged. This process ends with releasing \(\text{SO}_4^{2-}\) due to nucleophilic attack by water molecules. The research conducted by Borda et al. (2003) also confirms the release of
sulfate from the surface. However, they do not rule out the possible existence of a sulfite-like species. Based on measurements done by Rintoul et al. (1997) and Sato et al. (1985) on sulfate, the Raman spectra shows a strong $\nu_{\text{sym}}$ (SO) band at 991 cm$^{-1}$ for solid and 978 cm$^{-1}$ for solution species. Li and Wadsworth (1993) were expecting to observe this band to occur at approximately 985 cm$^{-1}$ by passing large quantities of charge during oxidation of pyrite. Similar to this work, I did not observe any bands in the acquired spectra of the samples in that region. In case of presence of sulfite on the surface of pyrite, a strong $\nu_{\text{sym}}$ (SO) band at 984 cm$^{-1}$ for solid and 962 cm$^{-1}$ for solution was expected to be observed, but none were acquired.

Several studies have reported elemental sulfur in considerable quantities as a product of pyrite oxidation (McGuire et al., 2001; Sasaki et al., 1995; Schippers et al., 1996; Xu and Schoonen, 1995).

As Luther (1997) explains, reaction (R6.2) is a reversible equilibrium depending on the pH of the solution. In acidic environments, the equilibrium is to the right; thus, $S_8$ and bisulfite form. Therefore, for the case in which all of the thiosulfate decomposes without reacting with ferric ions, half of the sulfur will become bisulfite while the other half precipitates as elemental sulfur as follows:

$$8S_2O_3^{2−} + 8H^+ \rightarrow S_8 + 8HSO_3^-$$  \hspace{1cm} (R6.3)

However, Fe$^{3+}$ does react with bisulfite and thiosulfate to form sulfate and tetrathionate, respectively. Therefore there is more than one pathway for pyrite oxidation which may or may not depend on the fate of thiosulfate-like surface species. Druschel and Borda (2006), based on the increasing evidence accumulated from the literature, concluded that pyrite oxidation may occur via several different reaction pathways. One pathway involves thiosulfate, in which oxidation occurs at the surface to form an Fe–SSO$_3$ surface species, which may either occur as the Fe–S bond breaks and thiosulfate is released, or as the S–S bond breaks and sulfite is released. In either of these cases the released products react finally to form sulfate in solution. The sulfide-polysulfide-elemental sulfur pathway is based on the release of sulfide or polysulfide and may or may not be related to the thiosulfate path. There is also a defect/photochemically-
driven pathway in which holes or radicals drive pyrite reactivity to interact with surface waters and succeeding sulfur oxidation to sulfate.

In order to determine quantitatively the possible sulfoxy anions formed on the surface of pyrite, the bands were compared with the tables prepared by Sato et al. (1985) for characteristic Raman bands of the sulfoxy anions. The two best candidates are thiosulfate and tetrathionate, showing a band in the 440–473 cm$^{-1}$ range. However, as also mentioned by Lehmann et al. (2000), a band at 995 cm$^{-1}$, a symmetric S–O stretch, is expected to appear with medium intensity, if the identified band resulted because of thiosulfate ions. Lehmann et al. (2000) used the observation of Freedman and Straughan (1971), that thiosulfate complexation via oxygen displaces the S–O stretch to lower wavenumbers, to support their postulation that adsorbed thiosulfate ions on the pyrite surface broaden the band and cause a reduction in the intensity of this band.

Parker (2005) first considers the claim of Lehmann et al. (2000) of identification of an adsorbed thiosulfate layer using normal Raman spectroscopy to be very unlikely, due to the high rotation speed of the electrode and absence of an S–O stretch. But later in her thesis, she admits that the attribution of Lehmann et al. (2000) of the $\nu$(SS) mode to thiosulfate was correct, and the lack of observation of the S–O stretch can be attributed to a loss of symmetry, through adsorption or electrostatic field effects, or even to instrumental interference such as cell window/filter ripple.

In this study, similar to the study done by Lehmann et al. (2000), it cannot be concluded with any certainty that thiosulfate ions or tetrathionate ions have been directly observed in these spectra. However, in 1998, Awatani and McQuillan published a paper in which they reported identification of adsorbed thiosulfate on the surface of cadmium sulfide using vibrational spectroscopy. They claimed that the oxidation of sulfide ions at CdS surfaces proceed via a strongly adsorbed thiosulfate intermediate, which is gradually converted to weakly adsorbed sulfate ions.

In one study, it was claimed by Sasaki et al. (1995) that bands in this range (440–473 cm$^{-1}$), in a spectrum acquired on electrochemically oxidized pyrite, disappeared once
the sample was immersed in cyclohexane (which selectively dissolves sulfur but not polysulfide) and they considered it to be noise. However, the paper would appear to be over-ambitious in its claims, considering that the Raman spectra presented in their paper had poor spectral resolution, identification of this broad range of bands was difficult to begin with, and the bands were still apparent even after immersion in cyclohexane; therefore, their results need to be interpreted with caution. In contrast to the study of Sasaki et al. (1995), Mycroft et al. (1990) used vacuum technique to evaporate the sulfur from oxidized pyrite surfaces. They reported that Raman bands assigned to elemental sulfur disappeared and only the broad range of bands assigned to polysulfide bands remained.

Parker and Hope (2010) observed a similar band at frequency of 452 cm\(^{-1}\) and assigned it to \(\nu(\text{SS})\) vibration and associated it to a laser induced product. These experiments were conducted under 442 nm laser irradiation, which is different from the wavenumber applied in this study. They did not report any Raman bands assigned to the bending modes \(\delta(\text{SSS})\). Thus, they believe that the laser induced phase was polymeric sulfur \((S_\mu)\).

Much controversy remains over the identity of the band observed in the 440–473 cm\(^{-1}\). My observations and the bulk of the literature support the general proposition that this band is either due to polysulfides or sulfoxy anions adsorbed to the pyrite surface as opposed to noise or laser-induced polymeric sulfur. In either case, most authors believe that this band is likely a sign of an intermediate product of pyrite oxidation. Not observing this band in pyrite #4 is an indication that pyrite oxidation has been completed and this shows that pyrite #4 has not been galvanically protected.

Whereas in pyrite #4, chalcopyrite leaching has been successful since the chalcopyrite is preferentially oxidised in the early stages of the leach, while an indication of intermediate product formation is observed at longer times in the form of sulfur products.
CHAPTER 7: Investigation of Pyrite Electrodes Modified by Gold and Silver Nanoparticles

Previous chapters in this thesis showed that natural pyrite samples with various chemical compositions can catalyze the ferric reduction reaction differently and this behavior was attributed to a difference in the interfacial charge transfer between semiconductor electrode and redox species associated with those samples. This research has consistently highlighted that charge transfer between pyrite and the redox couple in the solution is the key in chalcopyrite leaching kinetics. Questions have been raised about finding a way to modify this charge transfer in pyrite samples and the nature of its mechanism. The excellent physical properties of gold and silver nanoparticles were employed to modify charge transfer properties of pyrite electrodes.

The modified pyrite was investigated using Electrochemical Impedance Spectroscopy (EIS). Electrodes were prepared from both natural and modified pyrite samples and were modeled using an equivalent circuit (EC) based on the EIS data.

7.1 UV-Vis Spectroscopy Investigation of Colloidal Solutions

Based on variations in SPR response, UV-Vis spectra of the colloidal precious metal suspensions were fitted using the Mie-Gans models to examine particle size, concentration and the fraction of non-spherical particles. While the Mie model accounts only for spherical particles (usually synthesized by laser ablation), many routes for Au nanoparticle synthesis also form aggregates with nonspherical morphologies, and it has been shown that the results obtained from analyzes with Mie-Gans models compare well with TEM measurements (Amendola et al., 2006). The fitting program is freeware and the evaluation method, fitting procedure and models are thoroughly covered in a paper published by Amendola and Meneghetti (2009). This fitting program allows for simple calibration of the model and it can be adapted to other nanoparticles with an SPR in the UV-Vis range, enabling analysis of Ag nanoparticles.
Figure 7.1 a shows the UV-Vis experimental spectrum of Au nanoparticles, the SPR maximum is observed near 530 nm. The Mie-Gans fitting of the UV-Vis spectrum produces an average radius of $R = 10.1$ nm. Of Au nanoparticles, 41% were spheres and the other 59% are estimated to be prolate spheroid of aspect ratio $a/b$ with a Gaussian distribution of aspect ratio centered on 1 with a standard deviation equal to 1.86.

Figure 7.1 b shows the UV-Vis spectrum of Ag nanoparticles, where the SPR maximum is observed near 400 nm. The Mie-Gans fitting yields an average radius of $R = 13.4$ nm. 66% of Ag nanoparticles are estimated to be spheroids with a Gaussian distribution of aspect ratio with a standard deviation equal to 1.70.

Instability during nanoparticle growth or the improper ratio of the reactants can cause aggregation during or after synthesis. This phenomenon can cause the SPR to shift to longer wavelengths and produce a color change in the colloids. This effect can be observed in the spectra by the presence of extra peaks along with a reduction in the intensity of the SPR peak.
Figure 7.1  UV-Vis absorption spectrum of a) Au, and sol b) Ag sol.
7.2 Electrochemical Impedance Spectroscopy of Modified Pyrite Electrodes

Electrochemical Impedance Spectroscopy (EIS) studies on pyrite single particle microelectrodes were conducted on one natural pyrite sample (pyrite#4) and 2 modified pyrite samples, one with Au nanoparticles and the other with Ag nanoparticles at 420 mV vs. SCE. Same equivalent circuit used in chapter 5 was employed here to model the acquired impedance spectra of the modified pyrite samples. Nyquist plots, Bode plots and impedance error measurements, presented in Figure 7.2 and Figure 7.3 show a good fit of the model and the measured datasets. A Chi-Squared ($\chi^2$) value equal to $1.20 \times 10^{-3}$ for silver modified pyrite and $4.38 \times 10^{-4}$ for gold modified pyrite is an indication for the goodness of the fit. Table 7.1 shows the average values for each circuit element before and after modifying with nanoparticles.
Figure 7.2 Nyquist and Bode plots showing the fit of $R(QR)(CR)$ model and impedance error measurement of modified pyrite sample P#4-AgNP-1 using microelectrode (solution 0.5M H$_2$SO$_4$, 0.005M Fe$_2$(SO$_4$)$_3$ and 0.005M Fe(SO$_4$)).
Figure 7.3 Nyquist and Bode plots showing the fit of R(QR)(CR) model and impedance error measurement of modified pyrite sample P#4-AuNP-1 using microelectrode (solution 0.5M H$_2$SO$_4$, 0.005M Fe$_2$(SO$_4$)$_3$ and 0.005M Fe(SO$_4$)).
Table 7.1  Average values of elements of equivalent circuit $R_{sol}(R_{ct}Q)(C_{sc}R_{ss})$ shown in Figure 5.5 based on 10 samples for each pyrite type.

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<th>Pyrite type</th>
<th>$R_{sol}$ (Ωcm$^2$)</th>
<th>$R_{ct}$ (Ωcm$^2$)</th>
<th>$Q-Y_0$ (Ωs$^{-n}$)</th>
<th>$Q-n$</th>
<th>$C_{sc}$ (Fcm$^{-2}$)</th>
<th>$R_{ss}$ (Ωcm$^2$)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P#4</td>
<td>9.6</td>
<td>16.27×10$^3$</td>
<td>0.9×10$^{-4}$</td>
<td>0.72</td>
<td>-</td>
<td>-</td>
<td>5.46×10$^{-3}$</td>
</tr>
<tr>
<td>P#4-Ag NP</td>
<td>14.4</td>
<td>0.93×10$^3$</td>
<td>2.8×10$^{-4}$</td>
<td>0.74</td>
<td>6×10$^{-3}$</td>
<td>0.70×10$^3$</td>
<td>1.31×10$^{-3}$</td>
</tr>
<tr>
<td>P#4-Au NP</td>
<td>11.6</td>
<td>0.87×10$^3$</td>
<td>2.4×10$^{-4}$</td>
<td>0.75</td>
<td>8×10$^{-3}$</td>
<td>0.54×10$^3$</td>
<td>4.72×10$^{-3}$</td>
</tr>
</tbody>
</table>

Figure 7.4 compares the statistical representation of the measured spectra of all three types of pyrite electrodes. From the confidence intervals it can be suggested that modifying the pyrite electrode with the Au and Ag nanoparticles decreases the charge transfer resistance.

Electron transport via quantum dots is closely associated to the resonant tunneling phenomenon. This marked decrease in resistance can be rationalized by fast electronic transport between nanoparticles and the pyrite surface due to the resonant tunneling process through localized levels wiring the nanoparticle to the electrode.

In this case it is possible that resonant tunneling is occurring, referring to tunneling in which the electron transmission coefficient through a structure is sharply peaked about certain energies (Ferry et al., 2009). However, other possible mechanisms cannot be ruled out.
Figure 7.4  The mean values and error bar representation of equivalent analog circuit elements for natural pyrite, pyrite modified with Au nanoparticles and pyrite modified with Ag nanoparticles. Error bars represent the 95% confidence interval for the mean value shown by diamonds, n=10.
CHAPTER 8: Conclusions and recommendations

8.1 Summary and Conclusions

As addressed in the introductory chapter, satisfying the high global consumption and steadily growing demand of copper is a key challenge to be tackled by the metals extraction industry. The opportunity to make the largest copper resource on earth available, through the hydrometallurgical treatment of chalcopyrite, is key to maintaining the necessary production. Galvanox™ utilizes the galvanic interaction between pyrite and chalcopyrite to catalyze chalcopyrite dissolution by providing an alternative surface area for the ferric reduction reaction and has proven to be a highly promising option. However, over the course of extensive bench test work, some inconsistencies in the behavior of pyrite samples originating from different geographical locations has become apparent.

The research work presented in this thesis addresses these inconsistencies, exploring the reasons behind them through examination of various pyrite samples and their associated behavior. Electrochemical techniques were employed in conjunction with batch leaching tests to obtain fundamental insights on the mechanism behind the catalytic effect of pyrite on chalcopyrite dissolution in the Galvanox™ process. In order to investigate industrial concentrates and not to be confined to scientific samples, several novel methods for preparation of working electrodes were developed.

The data provides further evidence that pyrite samples from various sources can influence the rate of chalcopyrite leaching differently, because different pyrite samples support different rates of ferric reduction.

An electrochemical study was conducted on both macro and ground samples of chalcopyrite, either untreated or during the course of batch Galvanox™ leaching tests. Solid paraffin-based carbon paste electrodes (SPCPE) made from ground mineral samples were used as working electrodes to investigate details of the chalcopyrite dissolution process during pyrite-assisted leaching, in which they displayed excellent reproducibility. Cyclic voltammetry was combined with chemical and SEM/EDX analysis...
of Galvanox™ leaching residues. Chalcopyrite dissolution is a complex process which involves many intermediate reactions, one of which produces elemental sulfur on the mineral surface. Two different sulfur morphologies were observed on the surface of chalcopyrite in the presence and absence of pyrite. This difference in morphology can be considered as an indication of the rate and extent of leaching. It is hypothesized that pyrite assists the dissolution of copper from chalcopyrite by a galvanic effect, which is but one of several potential effects that pyrite may have on chalcopyrite leaching. Comparison of ferric reduction peaks in the voltammograms of pyrite and chalcopyrite indicates that pyrite is more electro-catalytic for the reduction of ferric than chalcopyrite. Thus adding pyrite to the leaching process can facilitate the transfer of electrons in the ferric reduction reaction, which considerably enhances the kinetics of chalcopyrite leaching in ferric sulfate solutions. Partially leached chalcopyrite particles showed a declining ability to reduce ferric with increased leaching time, suggesting that chalcopyrite surfaces continue to evolve toward a passive state, even in the presence of pyrite. The evidence from this study suggests that pyrite facilitates ferric reduction and acts as the cathode in the chalcopyrite oxidation process.

A microelectrode technique was successfully applied to cyclic voltammetry, EIS and Mott-Schottky methods, which generated reproducible results. The most obvious finding to emerge from this study is that pyrite with the highest enhancing effect on leaching kinetics is a better electron conductor than other types of pyrite, since the calculated values of charge transfer resistance were lower. Thus, this pyrite offers a better catalytic surface for ferric reduction, which is the key to the kinetics of chalcopyrite leaching in the presence of pyrite.

Investigation of the semiconducting properties of pyrite samples from different geographical locations showed differences in the calculated values of some parameters. The values of flat band potential and donor density are shown to be higher in pyrite samples with the highest enhancing effect on chalcopyrite leaching kinetics and lower in pyrite samples with the lowest enhancing effect. On the other hand, pyrite samples with the lowest enhancing effect on chalcopyrite leaching show the highest value for the depletion layer width, which decreases in pyrite samples with the lowest enhancing
effect. As the amount of impurities increases, the standard deviation of measured data points also increases, showing that the semiconducting properties of pyrite vary as functions of the level of impurities. This also affects the electrochemical performance of pyrite samples. All pyrite samples showed a change from $n$-type to $p$-type behavior with increasing potential to 0.65V. At this potential, the $p$-type semiconducting layer formed on the surface produces a P-N junction diode with the underlying pyrite that is reverse biased for passing an anodic current.

In order to unravel what occurs on the surface of chalcopyrite and pyrite during the course of Galvanox™ leaching and investigate if different sulfur species form on the surface of pyrite samples showing various enhancing behavior, Micro Raman spectroscopy was employed.

This surface study on the pyrite samples was taken after different periods of time during Galvanox™ leaching was conducted. It is concluded that the spectra collected from the surfaces of pyrite during pyrite-assisted chalcopyrite leaching are consistent with the existence of multiple sulfur species. Considering the complexity of pyrite oxidation, an accurate assignment of the sulfur species was not realistic. The presence of sulfur species other than S$_8$ at the pyrite surface is consistent with the multi-step oxidation of pyrite discussed in earlier studies. The presence of intermediate products of pyrite oxidation and the weaker S$_8$ Raman peaks on pyrite samples with the highest enhancing effect on the chalcopyrite leaching kinetics indicates that chalcopyrite is being preferentially oxidized increasing the rate of copper recovery. On the other hand, the exclusive existence of S$_8$ with more prominent Raman peaks, and its presence in all samples on the surface of pyrite samples with the lowest enhancing effect on the chalcopyrite leaching indicates completion of the oxidation reaction on the pyrite surface, a lack of cathodic protection, and consequently a lack of any enhancing effect on the kinetics of copper extraction from chalcopyrite.

An effort was made to modify pyrite to enhance its conductive properties and to further aid ferric reduction. The unique properties of gold and silver nanoparticles make them ideal for modifying pyrite electrodes. The dynamics of charge transfer across the
pyrite/electrolyte interface was investigated on both natural and modified pyrite samples. A reduction of several orders of magnitude in the charge transfer resistance was observed in EIS measurements of pyrite electrodes modified by Au and Ag NPs, suggesting that the activation energy for electron transfer across the semiconductor/electrolyte interface is significantly lower in their absence. This behavior is rationalized in terms of isoenergetic electron transport at the Fermi energy of the redox couple mediated by the presence of nanoparticles. The hypothesized phenomenon may resemble a resonant tunneling transport mechanism.

Combining the findings from the entire investigation it was found that in the absence of pyrite in the leach, the chalcopyrite loses the ability to reduce ferric. In the presence of pyrite, the catalytic ability of pyrite is largely dictated by ferric reduction on the surface of pyrite. Thus, ferric reduction is the key to copper dissolution from chalcopyrite, which is controlled by charge transfer at the pyrite/solution interface, and which can be enhanced by modifying the pyrite surface, such as with the addition of highly conductive nanoparticles.

8.2 Recommendations

Based on the research presented in this dissertation, some ideas are suggested for further investigation:

- Application of Solid Paraffin Carbon Paste Electrodes opens up the possibility of exploring a vast range of interactions between minerals. The use of such electrodes prepared from mixtures of chalcopyrite and pyrite is suggested. Another type of electrode could also be prepared in which a portion of the electrode surface is covered with pyrite and the rest is covered with chalcopyrite and in physical and electrical contact with each other. By this means the effect of the ratio of pyrite to chalcopyrite could be investigated. This electrode could be used for exploring the galvanic effect between other industrial minerals as well.

- Surface Enhanced Raman Spectroscopy (SERS), due to its high selectivity and rich spectral information through the formation of Au island films, can be widely used for detection of dissolution products on the submonolayer level of
chalcopyrite and pyrite surfaces. Thus, another possible direction for future research can be a surface study of chalcopyrite and pyrite surfaces during Galvanox™ leaching utilizing SERS.

- Synthesizing pyrite crystals doped with silver and gold utilizing chemical vapor transport techniques, and measuring their semiconducting properties, and using them in Galvanox™ leaching tests is recommended.

- Thin Film Rotating Ring Disk Electrodes (TF-RRDE) can be employed to investigate the electrochemical kinetics of the anodic and cathodic half-cell reactions and the effect of the galvanic couple between pyrite and chalcopyrite. In this study ground pyrite and chalcopyrite can be put onto polished glassy-carbon disks by applying 20 mL of a well-dispersed ink. Mineral dispersions can be prepared by ultrasonically dispersing 20–50 mg of catalyst in 50 ml of an aqueous solution containing 10–20 mL of isopropanol and 0.2 mL of a 5 wt. % Nafion.

- The effect of p-type semiconducting layer formed on the surface of pyrite and the resulting p-n junction diode with the underlying pyrite on chalcopyrite leaching performance or catalytic ability of pyrite on the ferric reduction can be investigated.
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