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SEMICONDUCTOR ELECTROCHEMISTRY OF COAL PYRITE

Technical Progress Report

January - March 1993

by

K. Osseo-Asare and Dawei Wei

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ABSTRACT

The work performed during this quarter focuses on the synthesis of pyrite in aqueous solutions at room temperature and atmospheric pressure. The experimental results show that the initial product from the reaction between ferrous ions and sulfide ions is X-ray amorphous iron sulfide, and the final product is mackinawite from this reaction. Both amorphous iron sulfide and mackinawite in wet states are oxidized quickly in air to γ -FeOOH. Pyrite can form in aqueous solution through a simple path from a reaction between ferric ions and sulfide ions at room temperature within 9 days. It is believed that a redox reaction occurs between ferric and sulfide ions to form ferrous ions and elemental sulfur. The Fe^{2+} , S^{2-} ions and elemental sulfur, S^0 , in the system can then react with each other to form pyrite. This pathway of pyrite formation can be used in synthesizing nanoparticles of pyrite in microemulsions.

PROJECT OBJECTIVES

This project seeks to advance the fundamental understanding of the physico-chemical processes occurring at the pyrite/aqueous interface, in the context of coal cleaning, coal desulfurization, and acid mine drainage. A novel approach to the study of pyrite aqueous electrochemistry is proposed, based on the use of both synthetic and natural (i.e. coal-derived) pyrite specimens, the utilization of pyrite both in the form of micro (i.e. colloidal and subcolloidal) and macro (i.e. rotating ring disk) electrodes, and the application of in-situ direct electroanalytical and spectroelectrochemical characterization techniques. Central to this research is the recognition that pyrite is a semiconductor material. (Photo) electrochemical experiments will be conducted to unravel the mechanisms of anodic and

cathodic processes such as those associated with pyrite decomposition and the reduction of oxidants such as molecular oxygen and the ferric ion.

STATEMENT OF WORK

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

DESCRIPTION OF TECHNICAL PROGRESS:

INTRODUCTION

The pyrite / aqueous interface features prominently in many aspects of coal mining, processing and utilization (Meyers 1977; Nordstrom 1982; Mishra et al., 1987; Klimpel et al., 1988). Coals typically contain 1-4% sulfur, a major fraction of which may come from pyrite. Since the combustion of coal releases unacceptable quantities of sulfur-oxides into the atmosphere, coal-desulfurization is increasingly becoming a major component of coal processing technology (Mishra et al., 1987; Klimpel et al., 1988). Many of the currently available or proposed coal cleaning and desulfurization methods (e.g. froth flotation, oil flotation agglomeration, leaching) exploit physicochemical processes occurring at the

pyrite/aqueous interface. In addition to the deliberate utilization of pyrite /aqueous interfacial interactions in these industrial processes, there is also the natural (but unwanted) interfacial process of dissolution of pyrite that leads to the serious environmental problem of acid-mine drainage (Nordstrom 1982).

There have been numerous studies on the aqueous interfacial chemistry of pyrite, all aimed at understanding and controlling the behavior of this metal sulfide in various stages of coal and mineral processing, and excellent review articles have been written (Hiskey et al., 1982; Lawson 1982). In spite of the vast volume of the literature on pyrite aqueous chemistry, there is little agreement on the mechanisms of pyrite surface reactions. A proper understanding of the fundamental chemistry of the pyrite/aqueous system is needed if improved strategies are to be devised for enhancing/suppressing pyrite reactions for commercial exploitation in coal cleaning and desulfurization or in controlling the environmental hazards associated with these reactions.

The conventional approach to pyrite decomposition chemistry, based on the metal electrode model, has nearly exhausted its possibilities. The power and utility of the semiconductor electrochemical model of pyrite/aqueous systems has been suggested (Osseo-Asare 1992). A recent and rapidly developing branch of colloid science, i.e. the field of small particle research, has a potential application in the study of the semiconductor electrochemical model of this mineral since the use of pyrite microelectrodes of colloidal dimensions can offer new and exciting possibilities for investigations of these reactions. A number of studies have revealed that semiconductor particles undergo dramatic changes in their electronic energy levels as they attain colloidal to subcolloidal dimensions (Henglein 1989; Steigerwald et al., 1990). With decrease in particle size, the valence band descends to lower energies, while the conduction band rises to higher energies; that is, the energy gap (E_g) increases with decrease in particle size. The net result is that there is a significant size-dependence of the optical properties of semiconductor colloids, particularly for those materials with $E_g < 1.5$ eV (Becker et al., 1983; Weller et al., 1985). Therefore, the size

dependent optical properties can be exploited as a means of monitoring the decomposition processes of semiconductor particles. Furthermore, the successful detection of aqueous soluble species by a given analytical technique requires that these species be present at sufficiently high concentrations. Therefore in the effort to obtain quantitative information about the intermediate species in the pyrite/aqueous system, use of pyrite in a highly divided form would be advantageous since with ultrafine particles there would be an increase in the amount of reaction surface per given pyrite/aqueous mass ratio.

The work currently in progress in our laboratory seeks to synthesize nanoparticles of pyrite in water-in oil microemulsions by a novel technique (Fendler 1987; Leung et al., 1988; Hou et al., 1988; Ward et al., 1989; Osseo-Asare et al., 1990a, 1990b). Because of the complications associated with the pyrite formation process itself (Morse et al., 1987; Schoone et al., 1991; Luther 1991), the pyrite synthesis experiments are being performed first in aqueous solutions. The information and experience obtained from this study will be very useful in the subsequent effort to synthesize nanoparticles of pyrite in microemulsions.

PREVIOUS WORK

Many studies have shown that pyrite can be formed from aqueous solutions at low temperatures and atmospheric pressure (Allen et al., 1914; Berner 1964, 1969, 1970, 1984; Rickard 1969, 1975; Roberts 1969; Sweeney et al., 1973; Howarth 1979; Taylor et al., 1979; Tossell et al., 1981; Morse et al., 1987; Luther III 1991; Schoonen et al., 1991). A summary of published data is shown in Table 1. A diagrammatic summary of the major pathways of pyrite formation in aqueous solution is shown in Figure 1. It can be seen from Table 1 that the reaction of $\text{Fe}^{2+} + \text{S}^{2-} + \text{S}^0 \rightarrow \text{FeS}_2$ is a main path to form pyrite. However, this pathway may not be suitable for synthesizing nanoparticles of pyrite in microemulsion media, because the addition of solid elemental sulfur will introduce new complications. The reaction of $\text{Fe}^{2+} + \text{S}_n^{2-} \rightarrow \text{FeS}_2$ seems straightforward, but pure

TABLE 1. Summary of published data on FeS₂ formation at low temperature.

Starting materials	Temperature °C	pH	Aging time	Products	Ref.
FeCl ₂ + H ₂ S + S ⁰	25-60 °C	-	5 days	pyr	1
FeS + H ₂ S + S ⁰	65	7.9	14 days	pyr	2
Mack + S ⁰	40	8.0	-	pyr	3
Mack + H ₂ S	35	-	3 days	greig, mack, pyr	4
Mack + Na ₂ S _n	25	7.0	-	pyr, marcas	5
FeO.OH + H ₂ S	20-25	4	2 days	pyr, mack	6
FeO.OH+H ₂ S+S ^{0*}	25	6.5	26 days	pyr, S ⁰	7
FeSO ₄ + H ₂ S	40-42	3	25 days	pyr, marcas	6
FeSO ₄ + Na ₂ S _n	25	4.4-9.5	-	pyr, marcas	5
Fe ^{2+***} + Na ₂ S ₂	25	7.0	4 months	pyr	8
Fe ^{3+***} + Na ₂ S ₂	25	5.8	2 days	pyr	8
Fe(NH ₄) ₂ (SO ₄) ₂ +Na ₂ S ₄	65	7.3-7.6	18 days	pyr	9

* S⁰ was obtained from oxidizing H₂S by Fe³⁺.

** Fe²⁺ sources are FeCl₂, FeSO₄ and Fe(NH₄)₂(SO₄)₂.

***Fe³⁺ sources are FeCl₃ and Fe(NO₃)₃.

pyr = pyrite; mack = mackinawite; greig = greigite; marcas = marcasite; goeth = goethite.

1-Sweeney et al., 1973; 2-Berner 1969; 3-Rickard 1975; 4-Taylor et al., 1979;

5-Rickard 1969; 6-Berner 1964; 7- Roberts 1969; 8-Luther III 1991; 9-Schoonen et al., 1991.

FIGURE 1. Reaction pathways for pyrite formation.

pure chemicals of S_n^{2-} are not available for direct use, and the commercially obtained Na_2S_4 has been used to synthesize pyrite only under higher temperatures (75 °C, Murowchick et al., 1986; 65 °C, Schoonen et al., 1991). The objective of this study is to search for a straightforward pathway to synthesize pyrite in aqueous solution at ambient temperature. This pathway should be suitable for making nanoparticles of pyrite in microemulsions.

EXPERIMENTAL

Reagent grade ferrous salts ($FeCl_2 \cdot 4H_2O$, $FeSO_4 \cdot 7H_2O$, $Fe(NH_4)_2(SO_4)_2$) and ferric salt ($FeCl_3 \cdot 6H_2O$) obtained from Aldrich were used as iron sources. Sodium sulfide ($Na_2S \cdot 9H_2O$) and sodium thiosulfate ($Na_2S_2O_3$) from Aldrich were used as sulfur sources. Fe(II) and Fe(III) solutions with concentrations of 0.1 mol/l were made respectively by dissolving ferrous salts and ferric salt in oxygen-free distilled water containing 0.01 N HCl to prevent $Fe(OH)_2$ or $Fe(OH)_3$ precipitation. Sulfide and thiosulfate solutions with concentrations of 0.1 mol/l were made by dissolving Na_2S and $Na_2S_2O_3$ in oxygen-free distilled water respectively. The oxygen-free distilled water was prepared by bubbling purified N_2 in distilled water for at least 5 hours. All solutions were prepared daily. The pH of the reaction solutions was controlled by adjusting the pH of either the Fe or sulfur solution via small additions of concentrated HCl or NaOH. In the

case of $\text{pH} > 7$, NaOH was added to the sulfur solution, while for $\text{pH} < 7$, HCl was added to the Fe solution. The pH of the reaction mixture was measured immediately with a Model 701 A digital pH/mV meter (Orion Research) after the two solutions were mixed in a separate experiment.

The reactions between iron and sulfide ions in aqueous solution were carried out in a glove box with a nitrogen pressure maintained at about 20 to 30 psi. Iron solution (20 ml, 0.1 mol/l) was mixed with 20 ml, 0.1 mol/l sulfide solution in a 50 ml screwcapped vial in the glove box. The vial was shaken manually for a few seconds and then left open to the nitrogen atmosphere for 5 hours. After that, the vial was sealed and left in the glove box for aging until the moment for examination. The temperature for the reactions was not specially controlled. The room temperature was around 25 °C.

A simple technique was developed to obtain X-ray diffractograms with a minimum of preparation time. The solid precipitate was separated from liquid by filtration. The wet solid was placed on a glass plate and stored in a plastic bag filled with nitrogen up to the moment of examination. The samples thus prepared are easily oxidized. However, this tendency did not affect the identification of the solid phases, as shown below. The diffractograms were obtained at medium scan rates and high sensitivity (Rigaku Geigerflex, CuK α radiation, 5° (2 θ)/min., 200 cps) to minimize the oxidation and enhance small peaks.

RESULTS AND DISCUSSION

The experimental results are summarized in Table 2. It can be seen that neither ferrous ions nor ferric ions can react with sodium thiosulfate to form iron sulfides. The reactions between ferrous ions and sulfide ions can only form mackinawite within the duration of the experiment. However, pyrite can be produced from the reaction between ferric and sulfide ions in aqueous solution at room temperature.

The X-ray diffractograms for runs 15#, 16#, and 19# are shown in Figure 2, 3 and 4, and an example of X-ray analysis of the synthetic mackinawite (run 16#) is shown in

TABLE 2. Summary of the experimental results for making pyrite at 25 °C.

Run	Source of Fe	Source of S	Reaction pH	Aging time	Products
15#	FeCl ₂	Na ₂ S	7.3	9 days	mackinawite
16#	FeSO ₄	Na ₂ S	7.4	9 days	mackinawite
19#	Fe(NH ₄) ₂ (SO ₄) ₂	Na ₂ S	7.5	9 days	mackinawite
17 #	FeCl ₃	Na ₂ S	6.5	9 days	pyrite
2#	FeCl ₂	Na ₂ S ₂ O ₃	6.2	9 days	no precipitate
4#	FeCl ₃	Na ₂ S ₂ O ₃	5.0	9 days	no precipitate
25 #	FeCl ₂	Na ₂ S	7.3	immediate	amorphous FeS
26#	FeCl ₃	Na ₂ S	6.5	immediate	amorphous FeS

Table 3. It can be seen that the d-spacing values of mackinawite obtained in this study are in good agreement with those obtained by Rickard (1969) and Bayliss et al.(1986). To identify the other peaks, which are not due to mackinawite, on the diffractograms in Figures 2, 3 and 4, a sample from run 16# was exposed in air for oxidation. The X-ray diffractograms for run 16#, which was oxidized in air for 30 minutes and 5 hours are shown in Figure 5 and 6 respectively. The X-ray data analysis shown in Table 4 indicates that the other peaks shown on the diffractograms are due to the presence of γ -FeOOH (lepidocrocite). This also suggests that the wet material of mackinawite oxidizes rapidly in air, as found by Berner (1962). The other properties of synthetic mackinawite are: black color when wet and soluble in concentrated HCl.

The X-ray diffractogram for run 17# is shown in Figure 7 and the X-ray analysis of the synthetic pyrite is shown in Table 5. Synthetic pyrite is black brown in color when wet, but it does not dissolve in concentrated HCl.

TABLE 3. X-ray data for synthetic mackinawite of run 16#.

Synthetic mackinawite				Natural mackinawite	
This study		Rickard (1969)		JCPDS 15-37*	
d Å	I	d Å	I	d Å	I
5.03	80	5.03	vs	5.03	100
2.97	80	2.97	s	2.97	80
2.60	40	2.60	w	2.60	5
2.31	80	2.28	m	2.31	80
-	-	1.838	mw	1.838	40
1.823	100	1.809	vs	1.808	80
1.725	40	1.720	mw	1.725	40
-	-	-	-	1.674	20
1.565	30	1.564	m	1.562	30
1.525	30	-	-	1.524	20
1.401	20	1.403	vm	1.409	20
1.302	30	1.298	mw	1.300	30
1.259	20	1.267	mw	1.258	30
-	-	-	-	1.240	40
1.190	20	1.194	vw	1.190	5
-	-	-	-	1.174	5
1.134	20	1.129	w	1.133	30
-	-	1.055	mw	1.055	60

* Bayliss et al., 1986.

vs = very strong; s = strong; ms = medium strong; m = medium; mw = medium weak;
w = weak; vw = very weak.

TABLE 4. X-ray data for γ -FeOOH (run 16# sample oxidized for 5 hours).

This study		JCPDS 8-98*	
d Å	I	d Å	I
6.28	80	6.26	100
3.29	100	3.29	90
2.46	90	2.47	80
2.36	30	2.36	20
2.09	20	2.09	20
1.937	60	1.937	70
1.848	20	1.848	20
1.733	30	1.732	40
1.563	20	1.566	20
-	-	1.535	20
1.523	30	1.524	40
-	-	1.449	10
1.434	20	1.433	20
1.388	20	1.389	10
1.369	20	1.367	30
1.266	10	1.261	10
-	-	1.213	10
1.199	10	1.196	20
1.187	10	1.189	20
-	-	1.100	20

* Bayliss et al., 1986.

TABLE 5. X-ray data for synthetic pyrite of run 17#.

This study		Rickard (1969)		JCPDS 15-37*	
d Å	I	d Å	I	d Å	I
3.164	30	3.34	mv	3.128	35
2.714	100	2.713	vs	2.709	85
2.429	50	2.424	s	2.428	65
2.227	30	2.212	s	2.212	50
1.914	40	1.918	ms	1.916	40
1.752	20	-	-	-	-
1.637	40	1.638	vs	1.633	100
-	-	1.565	mw	1.564	14
1.507	20	1.504	m	1.503	20
1.455	20	1.461	m	1.448	25
1.243	10	1.243	w	1.243	12
1.212	10	1.213	mw	1.211	14
1.183	10	1.183	mw	1.182	8
1.159	10	1.155	mw	1.155	6
1.108	10	1.106	mw	1.106	6

* Bayliss et al., 1986.

vs = very strong; s = strong; ms = medium strong; m = medium; mw = medium weak;
w = weak.

The initial products for the reactions both between ferrous and sulfide ions and between ferric and sulfide ions are X-ray amorphous iron sulfides as shown in Figures 8 and 9. These products oxidize readily to γ -FeOOH as shown in Figures 10 and 11.

It has been suggested by many investigators that pyrite formation is a two step process (Allen et al., 1914; Berner, 1964, 1967, 1969, 1970; Rickard, 1969, 1975; Roberts et al., 1969; Skripchenko, 1969; Sweeney and Kaplan, 1973; Goldhaber and Kaplan, 1974, Feld, 1977; Schoonen and Barnes, 1991). In the first step, an iron monosulfide precursor, FeS, forms via the reaction between aqueous sulfide and aqueous ferrous iron species:

In the second step, the iron monosulfide precursor is converted to pyrite in the presence of elemental sulfur (or polysulfide ions) and excess hydrogen sulfide:

Under the conditions used to form pyrite in this study, a redox reaction occurs initially between the ferric ions and the sulfide ions:

Thus both ferrous ions and elemental sulfur are available in the system. The presence of ferrous ions, sulfide ions and elemental sulfur produced pyrite in this system:

It is noted that this path of pyrite formation is quite simple and straightforward. A detailed study of this reaction will provide more information on the formation mechanism of pyrite,

and this will be useful in the planned synthesis of nanoparticles of pyrite in microemulsions.

CONCLUSIONS

Based on the experimental results and discussion, we can conclude that the initial product from the reaction between ferrous ions and sulfide ions is X-ray amorphous iron sulfide, and the final product is mackinawite from this reaction. Both amorphous iron sulfide and mackinawite in wet states are oxidized quickly in air to γ -FeOOH. Pyrite can form in aqueous solution through a simple synthesis protocol. It forms from a reaction between ferric ions and sulfide ions at room temperature within 9 days. It is believed that a redox reaction occurs between ferric and sulfide ions to form ferrous ions and elemental sulfur. The presence of Fe^{2+} , S^{2-} and S^0 in the system makes the formation of pyrite feasible. This pathway to pyrite formation will be used in synthesizing nanoparticles of pyrite in microemulsions.

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FIGURE 2. X-ray diffractogram of run 15#.

FIGURE 3. X-ray diffractogram of run 16#.

FIGURE 4. X-ray diffractogram of run 19#.

FIGURE 5. X-ray diffractogram of run 16# oxidized in air for 30 minutes.

FIGURE 6. X-ray diffractogram of run 16# oxidized in air for 5 hours.

FIGURE 7. X-ray diffractogram of run 17#.

FIGURE 8. X-ray diffractogram of run 25#.

FIGURE 9. X-ray diffractogram of run 26#.

FIGURE 10. X-ray diffractogram of run 25# oxidized in air for 30 minutes.

FIGURE 11. X-ray diffractogram of run 26# oxidized in air for 30 minutes.

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