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SEMICONDUCTOR ELECTROCHEMISTRY OF COAL PYRITE**Technical Progress Report****April - June 1993**

by

K. Osseo-Asare and Dawei Wei**Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802****DISCLAIMER**

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ABSTRACT

Pyrite (FeS_2) and mackinawite (FeS) were synthesized successfully in aqueous solution at room temperature and atmospheric pressure. FeCl_2 and FeCl_3 were chosen as the sources of iron, and Na_2S , NaHS and Na_2S_4 as the sources of sulfur. Pyrite was made from the reaction between Fe(III) and Na_2S or NaHS within a few days of aging. Mackinawite was made from the reaction between Fe(II) and Na_2S at pH 7.3 within 4 days. The reaction between Fe(II) and NaHS produced a mixture of mackinawite and pyrite at pH 4.0 within 4 days. Using Na_2S_4 as the source of sulfur, no mackinawite was observed under the experimental conditions. A mixture of pyrite and elemental sulfur was obtained from the reaction between Fe(II) or Fe(III) and Na_2S_4 .

Particle size analysis by a transmission electron microscope (TEM) showed that pyrite formed from the reaction between Fe(III) and Na_2S or NaHS has an average diameter of $150\text{ }\mu\text{m}$. To reduce the particle size into nanosize range, pyrite is being made currently in our laboratory either in dispersed aqueous solution or in water-in-oil microemulsion.

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). The conventional approach to pyrite electrochemistry, 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. 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. It can be seen 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, 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 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).

TABLE 1. Summary of published data on FeS_2 formation at low temperature.

Starting materials	Temperature °C	pH	Aging time	Products	Ref.
$FeCl_2 + H_2S + S^0$	25-60 °C	-	5 days	pyr	1
$FeS + H_2S + S^0$	65	7.9	14 days	pyr	2
Mack + S^0	40	8.0	-	pyr	3
Mack + H_2S	35	-	3 days	greig, mack, pyr	4
Mack + Na_2S_n	25	7.0	-	pyr, marcas	5
$FeO.OH + H_2S$	20-25	4	2 days	pyr, mack	6
$FeO.OH + H_2S + S^{0*}$	25	6.5	26 days	pyr, S^0	7
$FeSO_4 + H_2S$	40-42	3	25 days	pyr, marcas	6
$FeSO_4 + Na_2S_n$	25	4.4-9.5	-	pyr, marcas	5
$Fe^{2+***} + Na_2S_2$	25	7.0	4 months	pyr	8
$Fe^{3+****} + Na_2S_2$	25	5.8	2 days	pyr	8
$Fe(NH_4)_2(SO_4)_2 + Na_2S_4$	65	7.3-7.6	18 days	pyr	9

* S^0 was obtained from oxidizing H_2S by Fe^{3+} .

** Fe^{2+} sources are $FeCl_2$, $FeSO_4$ and $Fe(NH_4)_2(SO_4)_2$.

*** Fe^{3+} sources are $FeCl_3$ and $Fe(NO_3)_3$.

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.

The work done during this period was to synthesize pyrite in aqueous solution at room temperature and atmospheric pressure by a simple and straightforward method. Further work will be done to make nanoparticles of pyrite either in dispersed aqueous solution or 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).

EXPERIMENTAL

Reagent grade ferrous salts ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and ferric salt ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) obtained from Aldrich were used as iron sources. Sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and sodium hydrosulfide ($\text{NaHS} \cdot x\text{H}_2\text{O}$) from Aldrich and sodium tetrasulfide (Na_2S_4) from Alfa 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 M HCl to prevent $\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$ precipitation. Sulfide solutions with concentrations of 0.1 mol/l were made by dissolving Na_2S , NaHS and Na_2S_4 in oxygen-free distilled water respectively. These solutions were diluted further with oxygen-free distilled water to obtain the required concentrations. 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 S 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 experiments of making iron sulfides were carried out in a 50 ml screwcapped vial in a glove box with a nitrogen pressure maintained at about 20 to 30 psi. Iron and sulfide solutions in two separate vials without caps were placed in the glove box for 1 hour to release possible oxygen content in the solutions. Then the two solutions were mixed in

one vial. The vial was shaken manually for a few seconds and left open to the nitrogen atmosphere for 5 hours. After that, the vial was sealed and stored 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.

An X-ray diffractometer (Rigaku Geigerflex) was used to identify the phases of the materials formed. A simple technique was developed to obtain X-ray diffraction sample with a minimum of preparation time (Osseo-Asare et al., 1993). The characterization of the particles was done using a Philips 420 T transmission electron microscope (TEM). Before taking the TEM sample from aqueous solution, the sealed vial was shaken manually for 1 minute to suspend the particles. The vial was then opened, and a sample of the suspension was collected with a micropipette. With the micropipette, a droplet of suspension was deposited on a carbon-coated copper grid, and TEM examination was performed immediately.

RESULTS AND DISCUSSION

The experimental results for making iron sulfide at room temperature, using different sources of sulfur, are summarized in Tables 2 to 4. The X-ray diffractograms of amorphous FeS, mackinawite, a mixture of mackinawite and pyrite, pyrite, elemental sulfur and a mixture of elemental sulfur and pyrite are shown in Figures 1 to 6. Table 2 shows the results using Na₂S as the source of sulfur (Osseo-Asare et al., 1993). It can be seen that the reaction between Fe(II) and Na₂S produces mackinawite at pH 7.3 within 4 days. The reaction between Fe(III) and Na₂S produces pyrite at pH from 4.3 to 6.5 within 7 to 9 days. Table 3 shows the results using NaHS as the source of sulfur. It shows that the reaction between Fe(II) and NaHS produces a mixture of mackinawite and pyrite at pH 4.0 within 4 days. Pyrite can be made from the reaction between Fe(III) and NaHS at pH from 3.2 to 4.6 within 2 to 5 days. The concentrations of Fe(III) and NaHS can go down to as low as 0.0017 mol/l and 0.0033 mol/l respectively. Using Na₂S₄ as the source of

TABLE 2. Summary of the experimental results for making iron sulfides at 25 °C using Na₂S as the source of S.

Run	Source of Fe and conc., M	Source of S and conc., M	pH	Aging time	Product
25#	FeCl ₂ , 0.05	Na ₂ S, 0.05	7.3	30 min.	Amorphous FeS
R-15#	FeCl ₂ , 0.05	Na ₂ S, 0.05	7.3	4 days	Mackinawite
26#	FeCl ₃ , 0.05	Na ₂ S, 0.05	6.5	30 min.	Amorphous FeS
42#	FeCl ₃ , 0.05	Na ₂ S, 0.05	4.3	7 days	Pyrite
R-17#	FeCl ₃ , 0.05	Na ₂ S, 0.05	4.8	7 days	Pyrite
17#	FeCl ₃ , 0.05	Na ₂ S, 0.05	6.5	9 days	Pyrite

TABLE 3. Summary of the experimental results for making iron sulfides at 25 °C using NaHS as the source of S.

Run	Source of Fe and conc., M	Source of S and conc., M	pH	Aging time	Product
67#	FeCl ₂ , 0.033	NaSH, 0.067	4.0	4 days	Mack, Pyr
47#	FeCl ₂ , 0.05	NaSH, 0.05	3.8	17 days	Pyr, Mack
65#	FeCl ₃ , 0.033	NaSH, 0.067	3.6	1 day	Amorphous FeS
58#	FeCl ₃ , 0.033	NaSH, 0.067	3.6	2 days	Pyrite
85#	FeCl ₃ , 0.067	NaSH, 0.13	3.2	2 days	Pyrite
83#	FeCl ₃ , 0.017	NaSH, 0.033	3.7	3 days	Pyrite
81#	FeCl ₃ , 0.0033	NaSH, 0.0067	4.4	5 days	Pyrite
86#	FeCl ₃ , 0.0017	NaSH, 0.0033	4.6	5 days	Pyrite

TABLE 4. Summary of the experimental results for making iron sulfides at 25 °C using Na₂S₄ as the source of S.

Run	Source of Fe and conc., M	Source of S and conc., M	pH	Aging time	Product
51#	FeCl ₂ , 0.067	Na ₂ S ₄ , 0.033	4.3	6 days	S ⁰ , Pyrite
R-36#	FeCl ₂ , 0.05	Na ₂ S ₄ , 0.05	6.5	17 days	Pyrite, S ⁰
**37#	FeCl ₂ , 0.033	Na ₂ S ₄ , 0.067	6.0	11 days	Pyrite, S ⁰
57#	FeCl ₃ , 0.067	Na ₂ S ₄ , 0.033	5.6	3 days	S ⁰
44#	FeCl ₃ , 0.05	Na ₂ S ₄ , 0.05	4.4	4 days	S ⁰ , Pyrite
35#	FeCl ₃ , 0.033	Na ₂ S ₄ , 0.067	4.7	11 days	S ⁰ , Pyrite
34#	FeCl ₃ , 0.033	Na ₂ S ₄ , 0.067	6.0	11 days	S ⁰ , Pyrite

sulfur (Table 4), neither mackinawite nor pure pyrite was produced from the reaction between Fe(II) or Fe(III) and Na₂S₄. The only product from these reactions is a mixture of elemental sulfur and pyrite.

Based on the experimental results shown above, the pathway of pyrite formation from the reaction between Fe(III) and NaHS is preferred because this reaction is fast and easy to control.

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; 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 of using Na₂S and NaHS as the sources of sulfur, 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 the path of pyrite formation from the reaction between Fe(III) and NaHS is quite simple and straightforward. However, the mechanisms of the reaction should be studied in detail. Also the mechanisms of the formation of a mixture of mackinawite and pyrite from Fe(II) and NaHS and the formation of a mixture of elemental sulfur and pyrite from Fe(II) or Fe(III) and Na₂S₄ are not understood, and needed to be investigated further.

The TEM photographs of the materials formed in this study are shown in Figures 7 to 10. It can be seen that pyrite is formed well from the reaction between Fe(III) and Na₂S or NaHS. The average diameter of the pyrite particles is about 100 to 200 μm. The particle sizes of the mixtures of mackinawite/pyrite and sulfur/pyrite are much smaller than pure pyrite, and the particle size of mackinawite is even much smaller.

CONCLUSIONS

Pyrite can be synthesized from the reaction between Fe(III) and Na₂S or NaHS in aqueous solution at room temperature and atmospheric pressure within a few 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(II), S⁰ and S²⁻ in the aqueous system makes the formation of pyrite feasible. The path of pyrite formation from Fe(III) and NaHS is preferred because this reaction is fast and easy to control. The average diameter of pyrite thus formed is about 150 μm. To reduce the particle size into the nanosize range, pyrite will be made either in dispersed aqueous solution or in water-in-oil microemulsion system. The nanosize particle of pyrite will then be used in the study of semiconductor electrochemistry of pyrite.

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FIGURE 1. X-ray diffractogram of run 65#.

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

FIGURE 3. X-ray diffractogram of run 47#.

FIGURE 4. X-ray diffractogram of run 58#.

FIGURE 5. X-ray diffractogram of run 57#.

FIGURE 6. X-ray diffractogram of run R-36#.

(A)

(B)

FIGURE 10. TEM photographs of (A): amorphous FeS (25#) and (B): g-FeOOH (25# after oxidizing in air for 30 minutes).

(A)

(B)

FIGURE 9. TEM photographs of elemental sulfur + pyrite. (A): 35# and (B): R-36#.

(A)

(B)

FIGURE 8. TEM photographs of (A): pyrite (58#) and (B): mackinawite+pyrite (47#).

(A)

(B)

FIGURE 7. TEM photographs of (A): pyrite (17#) and (B): mackinawite (R-15#).

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