DEC 9 1993

DOE/PC/91303--78

SEMICONDUCTOR ELECTROCHEMISTRY OF COAL PYRITE

Technical Progress Report

July - September 1993

by

K. Osseo-Asare and Dawei Wei

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**Prepared for the
United States Department of Energy**

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

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ABSTRACT

Pyrite (FeS_2) synthesis was studied in aqueous solution at room temperature and atmospheric pressure using ferric chloride (FeCl_3) and sodium hydrosulfide (NaHS) as reactants, and sodium hexametaphosphate ($(\text{NaPO}_3)_6$) as dispersant and crystal growth modifier. (to control the particle size of pyrite). The effects of the reaction pH and the concentrations of the reactants and the dispersant on the product characteristics were studied. The pH of the reaction system determines the chemical constitution of the products. Elemental sulfur is produced at pH 2.4. As pH increases, the reaction product becomes a mixture of elemental sulfur plus pyrite at pH 2.9. In the pH range of 3.6 to 5.7, pyrite is formed with a pseudospherical shape and a size of 2 μm . With further increase in pH, amorphous iron sulfides are obtained. Lowering the concentrations of the reactants decreases the particle size of pyrite in the earlier stages of the reaction. However the final particles have the same size irrespective of the initial concentrations of the reactants used in the study. Addition of the dispersant can change the properties of the products. The mechanism of the dispersant action is currently under investigation, in an effort to minimize particle aggregation and produce discrete nanosize pyrite particles.

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), as reviewed previously (Osseo-Asare et al., 1993a). 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).

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. The effects of the pH of the reaction and the concentrations of the reactants and the dispersant on the formation of pyrite were studied by means of TEM, SEM, EDX and X-ray diffraction techniques. Further research is in progress in an effort to produce nanoparticles of pyrite either in dispersed aqueous solution or in water-in-oil microemulsions (Fendler 1987; Leung et al., 1988; Hou et al., 1988; Ward et al., 1989; Osseo-Asare et al., 1990a, 1990b).

EXPERIMENTAL

Ferric chloride ($FeCl_3 \cdot 6H_2O$) and sodium hydrosulfide ($NaHS \cdot xH_2O$) from Aldrich were used as the iron and sulfur sources respectively. Sodium hexametaphosphate ($(NaPO_3)_6$) from Aldrich was used as dispersant. All chemicals were of reagent grade. Fe(III) solution with a concentration of 0.1 mol/l was made by dissolving the ferric salt in oxygen-free distilled water containing 0.01 M HCl to prevent $Fe(OH)_2$ or $Fe(OH)_3$ precipitation. Sulfide solution with a concentration of 0.1 mol/l was made by dissolving NaHS in oxygen-free distilled water. Sodium hexametaphosphate solution was prepared at 0.5 mol/l. 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. Ferric and sulfide solutions were prepared daily. The pH of the reaction solutions was controlled by adjusting the pH of either the ferric or sulfide solution via small additions of concentrated HCl or NaOH. 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 synthesis experiments were carried out in 50 ml screwcapped vials in a glove box with nitrogen pressure maintained at 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., 1993a). The characterization of the particles was done using a Philips 420 T transmission electron microscope (TEM) and a SX-40A scanning electron microscope (SEM). Before extracting a TEM sample from the 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. To prepare the SEM specimen, the precipitate in the vial was separated by centrifugation and then dried in a vacuum oven at room temperature. The dried solid material was then placed on a specimen mount and coated with gold. Energy dispersive x-ray (EDX) was used to detect the components of the material under TEM or SEM.

RESULTS AND DISCUSSION

The previous experimental results (Osseo-Asare et al., 1993b) show that pyrite can be synthesized from the reaction between FeCl_3 and NaHS in aqueous solution at room

temperature and atmospheric pressure within a few days. To investigate the effects of some key system variables on the particle size of pyrite, the experiments were conducted in which the reaction pH, as well as the concentrations of reactants and dispersant were varied systematically.

Reaction pH

Experiments were performed with 0.033 M FeCl₃ and 0.067 M NaHS at different pH values. The nature of the solid product was identified by x-ray diffraction as shown in Figures 1 to 4. The characterization of the particle morphology was made by SEM as shown in Figures 5 to 7. The elemental components of the products were detected by EDX as shown in Figures 8 to 12. The experimental results are summarized in Table 1.

TABLE 1. Effects of pH on the formation of pyrite.

Run#	pH	X-ray phase	Soluble in HCl	Particle size, μm
220	2.4	S ⁰	No	~6
221	2.9	S ⁰ +pyrite	No	~6(S ⁰)+~1(pyrite)
222	3.6	Pyrite	No	~2
223	4.3	Pyrite	No	~2
224	5.7	Pyrite	No	~2
225	7.2	Amorphous	Yes	/
226	9.8	Amorphous	Yes	/
227	11.8	Amorphous	Yes	/

[FeCl₃] = 0.033 M, [NaHS] = 0.067 M, aging for 5 days.

It can be seen that at pH 2.4 the product identified by x-ray diffraction (Figure 1) and EDX (Figure 8) is elemental sulfur. The particles of elemental sulfur thus formed have an irregular shape with a size about 6 μm (Figure 5A). At pH 2.9, the product is a mixture of elemental sulfur and pyrite (Figure 2). The SEM micrograph shows two kinds of particles (Figure 5B), small spherical particles and large irregular ones. Examined by a point detection of EDX, the large particles give a big sulfur peak, but a very small iron peak (Figure 9). However, the small particles give both large peaks of sulfur and iron (Figure 10). This indicates that the larger particles are elemental sulfur and the smaller ones are pyrite. As pH increases from 3.6 to 5.7, only pyrite is formed from the reaction, which can be seen from both x-ray diffraction (Figure 3) and EDX spectrum (Figure 11). The pyrite particles formed in the pH range from 3.6 to 5.7 are roughly spherical with a particle size of about 2 μm (Figures 6A, 7A, 7B). With further increase in pH to 7.2, the material formed from the reaction becomes x-ray amorphous as shown in Figure 4. The $\gamma\text{-FeOOH}$ peaks appear in the diffractogram since amorphous iron sulfides are easily oxidized (Osseo-Asare et al., 1993a). Analysis of the amorphous material by EDX shows that the main components are sulfur and iron (Figure 12). The morphology of the amorphous iron sulfides is shown in Figure 6B. All the experimental data show that the optimal pH range for pyrite formation is 3.6 to 5.7. In this pH range, pure pyrite with a particle size of 2 μm can be synthesized.

Effects of Reactant (FeCl_3 and NaHS) Concentration

The effects of variations in the reactant concentrations on the particle size were examined by changing the concentration of FeCl_3 from 6.7×10^{-2} M to 1.7×10^{-3} M and fixing the ratio of $[\text{FeCl}_3]$ to $[\text{NaSH}]$ as 1:2. The pH of the reaction mixtures was not controlled particularly because it was typically in the range of 3.2 to 4.6, where it is suitable to form pyrite as discussed above. As shown in Figure 13, pyrite with a particle size of 2 μm can be formed within 2 days when the concentration of FeCl_3 is higher than

1.7×10^{-2} M. On the other hand, the particle size is about 50 nm when the concentration of FeCl_3 is less than 6.7×10^{-3} M. However, if the aging time is long enough, 5 days for example, the particle size of pyrite becomes $2 \mu\text{m}$ for any initial concentration of reactants (Figure 14). The particle size of pyrite as a function of reactant concentration for different aging time is shown in Figure 15. These results show that the initial concentrations of the reactants do not affect the final particle size if the aging time is long enough. However, small particles can be obtained by lowering the initial concentration of the reactants in the early stage of the reaction. This implies that if one can control the growth of the particles at a certain stage of the reaction, it may be possible to synthesize discrete nanosize particles. In future experiments, decreasing the reaction rate, by lowering temperature or reactant concentration, will be further explored in an effort to achieve better control of particle size. It should be noted that the pyrite particles formed at low reactant concentration and short reaction time have a wide size distribution as shown in Figure 16.

Concentration of Dispersant $(\text{NaPO}_3)_6$

Sodium hexametaphosphate $(\text{NaPO}_3)_6$ has been widely used as a dispersant in the synthesis of nanosize particles in aqueous solution (Fojtik et al., 1984; Weller et al., 1985; Henglein 1989). In the work reported here, the effect of $(\text{NaPO}_3)_6$ on the product characteristics was studied by fixing the concentration of the reactants at 0.017 M FeCl_3 and 0.033 M NaHS. The $(\text{NaPO}_3)_6$ solution (2 ml) was added to the NaHS solution (20 ml) first, and then the FeCl_3 solution (10 ml) was added. At first an attempt was made to maintain the pH of the reaction mixture at 4.3, but this was abandoned in the cases where $(\text{NaPO}_3)_6$ addition exceeded 0.0125 M, since under these conditions no black precipitate formed if the pH was adjusted to 4.3. Hence, the pH of the reaction was not particularly controlled when the addition of $(\text{NaPO}_3)_6$ was higher than 0.0125 M.

The experiments show that the addition of $(\text{NaPO}_3)_6$ affects the reaction products dramatically. Disk-like precipitates were formed when the concentration of $(\text{NaPO}_3)_6$ was

less than 6.25×10^{-3} M. However, when the concentration of $(\text{NaPO}_3)_6$ was in excess of 1.25×10^{-2} M, black dispersed suspensions were observed. The SEM micrographs of the materials formed from the reaction with different concentrations of $(\text{NaPO}_3)_6$ are shown in Figures 17 to 19. Combining these results with the EDX data, it can be stated that pyrite is formed with a particle size of $2 \mu\text{m}$ when $(\text{NaPO}_3)_6$ concentration is less than 1.25×10^{-3} M (Figures 17A and B); At 6.25×10^{-3} M $(\text{NaPO}_3)_6$, the particle size of pyrite increases to $3 \mu\text{m}$ (Figure 18A); At 1.25×10^{-2} M $(\text{NaPO}_3)_6$, amorphous iron sulfides were obtained (Figure 18B); and at $(\text{NaPO}_3)_6$ concentrations of 3.13×10^{-2} M and above, elemental sulfur was formed (Figures 19A and B). Additional experiments are currently in progress aimed at obtaining a better understanding of the mechanism of action of the $(\text{NaPO}_3)_6$. Also, further experiments will be conducted in an attempt to prepare discrete and well dispersed nanosize pyrite particles.

CONCLUSIONS

The investigations of the effects of reaction pH, reactant concentrations, and dispersant addition on the formation of pyrite lead to the following conclusions:

1. The reaction pH in the FeCl_3 and NaHS system controls the final products of the reaction. Spherical particles of pyrite with a size of $2 \mu\text{m}$ were produced in the pH range from 3.6 to 5.7. At pH 2.4, elemental sulfur was observed with an irregular shape and a size of $6 \mu\text{m}$. A mixture of elemental sulfur and pyrite was obtained at pH 2.9. When pH was higher than 7.2, amorphous iron sulfides were formed.

2. Lowering of the concentration of reactants (FeCl_3 and NaHS) can decrease the particle size of pyrite only in the early stage of the reaction. The final particles have the same size for any initial concentration of the reactants. This implies that the fine particles of pyrite may be obtained if one can control the growth (or aggregation) of the pyrite particles in the early stage.

3. Addition of the dispersant sodium hexametaphosphate, $(\text{NaPO}_3)_6$, affects the products from the reaction of FeCl_3 and NaHS dramatically. The products change from pyrite, amorphous iron sulfides to elemental sulfur when the concentration of $(\text{NaPO}_3)_6$ is varied from 0 to 6.25×10^{-2} M.

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FIGURE 1. X-ray diffractogram of the product formed from 0.033 M FeCl₃ and 0.067 M NaHS at pH 2.4.

FIGURE 2 X-ray diffractogram of the product formed from 0.033 M FeCl₃ and 0.067 M NaHS at pH 2.9.

FIGURE 3. X-ray diffractogram of the product formed from 0.033 M FeCl₃ and 0.067 M NaHS at pH 4.3.

FIGURE 4. X-ray diffractogram of the product formed from 0.033 M FeCl₃ and 0.067 M NaHS at pH 7.2.

FIGURE 5. SEM photographs of (A) elemental sulfur formed at pH 2.4, and (B) elemental sulfur plus pyrite formed at pH 2.9.

FIGURE 6. SEM photographs of (A) pyrite formed at pH 4.3, and (B) amorphous FeS formed at pH 7.2.

FIGURE 7. SEM photographs of pyrite (A) formed at pH 3.6, and (B) formed at pH 5.7.

FIGURE 8. EDX spectrum of the product formed from 0.033 M FeCl_3 and 0.067 M NaHS at pH 2.4.

FIGURE 9. EDX spectrum of the product (large particles) formed from 0.033 M FeCl_3 and 0.067 M NaHS at pH 2.9.

FIGURE 10. EDX spectrum of the product (small particles) formed from 0.033 M FeCl_3 and 0.067 M NaHS at pH 2.9.

FIGURE 11. EDX spectrum of the product formed from 0.033 M FeCl_3 and 0.067 M NaHS at pH 4.3.

FIGURE 12. EDX spectrum of the product formed from 0.033 M FeCl_3 and 0.067 M NaHS at pH 7.2.

FIGURE 13. TEM photographs of pyrite formed from different concentrations of reactants for the aging time of 2 days.

(A)-0.067 M FeCl_3 , 0.134 M NaHS, pH 3.2; (B)-0.033 M FeCl_3 , 0.067 M NaHS, pH 3.5;
 (C)-0.017 M FeCl_3 , 0.033 M NaHS, pH 3.7; (D)-0.0067 M FeCl_3 , 0.0134 M NaHS, pH 4.1;
 (E)-0.0033 M FeCl_3 , 0.0067 M NaHS, pH 4.4; (F)-0.0017 M FeCl_3 , 0.0033 M NaHS, pH 4.6.

FIGURE 14. TEM photographs of pyrite formed from different concentrations of reactants for the aging time of 5 days.
 (A)-0.067 M FeCl_3 , 0.134 M NaHS , pH 3.2; (B)-0.033 M FeCl_3 , 0.067 M NaHS , pH 3.5;
 (C)-0.017 M FeCl_3 , 0.033 M NaHS , pH 3.7; (D)-0.0067 M FeCl_3 , 0.0134 M NaHS , pH 4.1;
 (E)-0.0033 M FeCl_3 , 0.0067 M NaHS , pH 4.4; (F)-0.0017 M FeCl_3 , 0.0033 M NaHS , pH 4.6.

FIGURE 15 Particle size as a function of reactant concentration at different aging times.

FIGURE 16 TEM photographs of pyrite for the aging time of 2 days.
0.0033 M FeCl_3 , 0.0067 M NaHS and pH 4.4.

FIGURE 17. SEM photographs of the materials formed from the reaction between 0.017 M FeCl_3 and 0.033 M NaHS . (A) no $(\text{NaPO}_3)_6$, and (B) 1.25×10^{-3} M $(\text{NaPO}_3)_6$ at pH 4.3.

FIGURE 18. SEM photographs of the materials formed from the reaction between 0.017 M FeCl_3 and 0.033 M NaHS . (A) 6.25×10^{-3} $(\text{NaPO}_3)_6$ at pH 4.3, and (B) 1.25×10^{-2} M $(\text{NaPO}_3)_6$ at pH 4.8.

FIGURE 19. SEM photographs of the materials formed from the reaction between 0.017 M FeCl_3 and 0.033 M NaHS . (A) 3.13×10^{-2} $(\text{NaPO}_3)_6$ at pH 5.7, and (B) 6.25×10^{-2} M $(\text{NaPO}_3)_6$ at pH 6.2.

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