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SEMICONDUCTOR ELECTROCHEMISTRY OF COAL PYRITE

Technical Progress Report

January - March 1992

by

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ABSTRACT

The work performed during this quarter falls into two categories: (a) The kinetics of iron(II) sulfide(FeS) formation from the reaction between ferrous ions and bisulfide ions in aqueous solution, and (b) Synthesis of FeS in a nonionic microemulsion. In the kinetic investigation, the rate of FeS formation was followed by using a stopped-flow technique, with u.v.-visible absorption detection. This technique could provide kinetic information in the time range from milliseconds to minutes. A black substance formed rapidly at first and its color decayed slowly as the time increased further. It is believed that this dark substance is $\text{Fe}(\text{HS})_2$ intermediate and that it subsequently converts to FeS. The $\text{Fe}^{2+}/\text{HS}^-$ reaction was pH-dependent; it was more likely to form $\text{Fe}(\text{HS})_2$ at about pH 7.4. Synthesis of FeS was carried out in the Polyoxyethylene nonylphenyl ether (NP-5)-Cyclohexane-Water microemulsion. The experimental results showed that the formation of FeS was mainly controlled by the local pH in the water pool, the mole ratio of water to surfactant and the temperature of the environment.

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 microelectrodes, (a) nanoparticle 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

1. Kinetics of Iron Sulfide (FeS) Formation in Aqueous Solution

It is generally accepted that pyrite formation is a two step process (Schoonen et al. 1991a). First of all, amorphous FeS forms via the reaction of Fe^{2+} with H_2S . Then

pyrite formation takes place in the presence of intermediate sulfur species, such as S_n^{2-} or $S_2O_3^{2-}$. Therefore, the study of the kinetics of FeS formation in aqueous solution can provide useful information towards understanding the formation of pyrite.

Iron sulfide, FeS, can be formed by the reaction between Fe^{2+} and S^{2-} solutions. A black color was observed immediately when the two solutions were contacted. It has been suggested by some authors (Allen, 1914; Berner, 1962; Berner, 1964; Berner, 1970; Schoonen et al. 1991a,b) that the first-formed black material is iron sulfide, with a formula of FeS; this material has been identified by means of X-ray diffraction and/or chemical analysis (Berner, 1975; Schoonen et al, 1991a,b).

However, an interesting observation was made in our laboratory. Immediately after the Fe^{2+} and S^{2-} solutions were mixed, the solution became dark black, then the black color decayed and changed to brown within a few minutes. In some specific cases, upon contact of the two solutions, the mixed solution became black immediately, but it became colorless in milliseconds. A similar observation was also made by Schoonen and Barnes (Schoonen et al., 1991a). It was found that the black precipitate formed at the interface of the droplet dissolved within seconds. It was suggested that this highly unstable black material was probably amorphous FeS. What is the black material formed immediately when the Fe^{2+} and S^{2-} solutions are contacted? Is it really FeS? This question is raised because the color change during the reaction at the first few seconds may indicate that something else forms before FeS. Furthermore, no experimental evidence has been presented to demonstrate the formation of FeS at the early stage of the reaction; the material analyzed minutes or even hours later may not be the material formed in the first few seconds or even few milliseconds. Most recently, Rickard

reported that the well known initial black precipitate was a neutral iron bisulfide intermediate and not FeS (Rickard, 1991).

In the work reported below, the pathway of FeS formation, i.e. an explanation for the black material, is sought on the basis of the experimental data obtained with a stopped-flow spectrofluorimeter which can provide reaction rate data in the millisecond to seconds time range.

EXPERIMENTAL

Reagent grade ferrous chloride (FeCl_2) and sodium sulfide (Na_2S) were obtained from Aldrich. Fresh solutions of FeCl_2 and Na_2S were prepared, using oxygen-free distilled water. The pH of the Fe^{2+} and S^{2-} solutions was controlled via small additions of concentrated HCl or NaOH solution. In the case of $\text{pH} < 7$, HCl was added to the Fe^{2+} solution, while for $\text{pH} > 7$, NaOH was added to the S^{2-} solution. The pH was measured immediately after the two solutions were mixed by means of a Model 701 A digital pH/mV meter (Orion Research).

Kinetic measurements were made by using a DX.17MV sequential stopped-flow spectrofluorimeter (Applied Photophysics). This instrument allowed one to mix the Fe^{2+} and S^{2-} solutions in an optical cell and the absorbance of the reaction mixture was recorded as a function of time at room temperature. Distilled water was taken as the reference solution and the zero absorbance was adjusted before each measurement. A wavelength of 500 nm was chosen to monitor $\text{Fe}(\text{HS})_2$ in the solution, according to the spectra shown in Figures 1 and 2.

FIGURE 1. Absorption spectra for the reaction between Fe^{2+} and S^{2-} . $[\text{Fe}^{2+}]_T = 5 \times 10^{-4} \text{M}$, $[\text{S}^{2-}]_T = 5 \times 10^{-4} \text{M}$, $\text{pH} = 7.4$, at 23°C .

FIGURE 2. Absorption spectra of the Fe^{2+} - S^{2-} reaction mixture. $[\text{Fe}^{2+}]_{\text{T}}=5 \times 10^{-4}\text{M}$, $[\text{S}^{2-}]_{\text{T}}=5 \times 10^{-4}\text{M}$, $\text{pH}=7.4$, at 23°C .

RESULTS AND DISCUSSION

Pathways for the formation of FeS

The formation of FeS may involve direct interaction between the Fe^{2+} ion and the S^{2-} ion, the HS^- ion and molecular H_2S (Pohl,1953; Roberts,1969; Schoonen et al.,1991c):

It is commonly accepted that FeS is the first-formed material resulting from the reactions above and it is the final product when no elemental sulfur is present in the system (Berner,1975; Roberts,1969).

Typical absorbance vs time results generated in the kinetic experiments are shown in Figure 3. The absorbance increases rapidly within the first few seconds (Figure 3-A), which means that a black material is formed as soon as the Fe^{2+} and S^{2-} solutions are mixed together. The absorbance subsequently decreases less rapidly as the time decreases (Figure 3-B), which indicates that the black material formed at first is decomposed to form another species.

The experimental results on the effect of pH on the absorbance are shown in Figure 4. The position of the peak suggests that the maximum formation of the black material occurs at about pH 7.4; furthermore, this black substance is unlikely to form at

FIGURE 3. Absorption spectra as a function of time for the reaction between Fe^{2+} and HS^- . $[\text{Fe}^{2+}]_{\text{T}} = 5 \times 10^{-4} \text{M}$, $[\text{S}^{2-}]_{\text{T}} = 5 \times 10^{-4} \text{M}$, $\text{pH} = 7.4$, at 23°C . A is a part of B taken within the first 4 seconds.

FIGURE 4. Absorbance as a function of pH after 5 seconds of reaction.

FIGURE 5. Logarithmic concentration diagram for $5 \times 10^{-4} \text{ M S(II)}$.

FIGURE 6. Logarithmic concentration diagram for $1 \times 10^{-4} \text{ M}$ Fe(II) (Fuerstenau 1976).

pH values below 5 or above 11. Examination of the S^{2-} - H_2O and Fe^{2+} - H_2O speciation diagrams shown in Figures 5 and 6 respectively indicates that HS^- is predominant above pH 7 while Fe^{2+} is predominant below pH 8. In the pH range from 7 to 8, both Fe^{2+} and HS^- are predominant so that the black material is most likely formed by Fe^{2+} and HS^- ions. Based on the activated complex theory, the pathway of the reaction can be postulated as

or alternatively (Pohl, 1954),

where $Fe(HS)_2$ and $Fe(HS)^+$ are the complex intermediates. According to Equations 4 and 5, the black material should be either $Fe(HS)_2$ or $Fe(HS)^+$. It is clear that for the formation of the complex intermediates, the pathway will follow Equation 4 when the reaction order is 2 with respect to HS^- . On the other hand, it will follow Equation 5 when the order is 1. Work is currently in progress to determine the rate law.

Based on the results and discussion above, it can be concluded that the formation of FeS is via the reaction between the Fe^{2+} ion and the HS^- ion. The black material formed in the first few seconds may be either $Fe(HS)_2$ or $Fe(HS)^+$, but not FeS.

2. Synthesis of FeS Nanoparticles in Microemulsions

The successful detection of aqueous soluble species by a given analytical technique requires that these species be present at sufficiently high concentrations. Therefore, in order to obtain quantitative information about the intermediate sulfur-oxy species, use of pyrite in a highly divided form would be advantageous. With ultrafine particles, there would be an increase in the amount of reactive surface per given pyrite/water mass ratio and this should help to increase the bulk concentration of the water-soluble reaction products.

In response to this need for ultrafine solid particles, a novel reverse microemulsion technique (Fendler, 1987; Leung et al., 1988; Hou et al., 1988; Ward et al., 1989; Osseo-Asare et al., 1990) is being investigated as a means of making FeS and FeS₂ nanoparticles. The particle size and distribution can be controlled by the major variables in the process.

EXPERIMENTAL

Reagent grade ferrous chloride(FeCl₂), sodium sulfide(Na₂S), polyoxyethylene nonylphenyl ether(4-(C₉H₁₉)C₆H₄O(CH₂CH₂)₄CH₂CH₂OH)(NP-5), cyclohexane(C₆H₁₂), and buffer solutions were obtained from Aldrich. Ferrous chloride and sodium sulfide served as reactants, NP-5 as surfactant and cyclohexane as organic phase. The experimental apparatus and the procedure are shown in Figure 7. NP-5/cyclohexane solution was prepared by mixing certain volumes of NP-5 and cyclohexane. When the buffer, S²⁻ and Fe²⁺ solutions were added to the NP-5/cyclohexane solution, the reverse

FIGURE 7. Experimental set-up for FeS nanoparticle synthesis in NP-5/cyclohexane/water microemulsion.

microemulsion was formed. The reaction leading to the formation of FeS takes place in the water pools in the microemulsion. The pH of the reaction was controlled by buffer solutions. The temperature was controlled by the water bath. Nitrogen gas was introduced into the system to prevent oxidation.

RESULTS AND DISCUSSION

The results of the preliminary experiments show that the main variables in the process are the mole ratio of water to surfactant, the concentrations of reactants, the pH of the buffer solution, and the reaction temperature. Experiments that explore the detailed effects of these variables are currently in progress.

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