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SEMICONDUCTOR ELECTROCHEMISTRY OF COAL PYRITE

Technical Progress Report

January - March 1994

by

K. Osseo-Asare and Dawei Wei

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ABSTRACT

Electrochemical and photoelectrochemical experiments have been conducted with synthetic pyrite particles as microelectrodes. The photocurrent collection experiments show that the photocurrent increases dramatically when the particles of pyrite are irradiated by light. It is believed that the increase of the photocurrent results from the increase of the electron concentration in the conduction band of pyrite under illumination. Polarization experiments show that the anodic currents increase under irradiation. This indicates that anodic dissolution of pyrite involves a hole transfer pathway. Illumination increases the concentration of minority carriers (holes), thus increasing the anodic dissolution rate.

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, and the utilization of pyrite both in the form of micro (i.e. colloidal and subcolloidal) and macro (i.e. rotating ring disk)-electrodes. Central to this research is the search for the relationship between the semiconductor properties of pyrite and the interfacial electrochemical behavior of this metal sulfide in aqueous systems. (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 electrochemical properties of the pyrite-aqueous system are important for many aspects of advanced coal processing, e.g., coal cleaning, coal desulfurization, and abatement of acid mine drainage.

Pyrite is widely recognized as an electronic conductor and its oxidation has been described by the metal corrosion model for many years (Peters and Majima, 1968; Biegler and Swift, 1979, Peters, 1992). However, more recent electrochemical and photoelectrochemical experiments (Mishra and Osseo-Asare, 1987, 1988, 1992; Ahmed and Giziewicz 1992) have shown that the dissolution rate of pyrite increases in the presence of illumination, which means that both electrons and holes participate in the interfacial electrochemical reactions.

Pyrite, like most metal sulfides, is a semiconductor; the band gap is 1 ± 0.2 eV (Marinace, 1954; Bither et al., 1968; Gupta et al., 1980; Ennaoui et al., 1986; Liu et al., 1988). However, the semiconductor dissolution model for pyrite has not been accepted commonly, since little work has been done on the effects of semiconductor properties of pyrite on its dissolution behavior. In this reporting period, electrochemical and photoelectrochemical experiments have been conducted to explore the relationship between the semiconductor properties of pyrite and the interfacial electrochemical behavior of this metal sulfide.

EXPERIMENTAL

The apparatus used in the electrochemical and photoelectrochemical is shown in Figure 1. The 100 ml Pyrex H-cell consists of two chambers separated by a fine porosity glass frit, as used by Ward et al.(1983), so that the pyrite particles are confined to the main chamber. A platinum grid inert electrode with area of 2 cm^2 and a saturated calomel reference electrode (SCE) are in the main chamber and a platinum grid counter electrode is in the other chamber. On the wall of the main chamber there is a flat window which allows the light to go into the cell directly. The light source is an Oriel 250 W halogen lamp. A water bath with 14 cm length is placed between the cell and the light to absorb the heat. During the experiments a prepurified nitrogen stream was bubbled through the cell and a magnetic stirrer was used to bring the pyrite particles into contact with the inert electrode. A model 273 Potentiostat /Galvanostat (EG&G Princeton Applied Research) with a model 352 corrosion analysis software was used to make the electrochemical measurements.

RESULTS AND DISCUSSION

Photocurrent Collection Experiments

The results of photocurrent collection experiments are shown in Figure 2 under the conditions of 1 M Na_2S , pH 13.0, with and without FeS_2 particles (70 mg, $\sim 2 \mu\text{m}$ in

diameter). The inert electrode was held at a potential at -0.67 V(SCE). It can be seen that illumination does not affect the current in the absence of pyrite (Curve 1 in Figure 2). However, in the presence of pyrite (Curve 2 in Figure 2), a low current is observed in the dark; when the light is switched on the anodic current increases dramatically, and it decreases when the light is off.

The processes of photocurrent generation can be illustrated in Figure 3, where E_c and E_v refer to the bottom of the conduction band and the top of the valence band respectively, and E_h refers to the potential of the inert electrode. At pH 13, E_c is equal to -0.58 V(SHE) or -0.82 V(SCE) (Chen et al., 1991). Since the potential of the inert electrode (-0.67 V (SCE)) is more positive than E_c , the electrons in the conduction band of pyrite can be caught by the inert electrode, resulting in anodic current. When the light, with an energy higher than the band gap of pyrite, is incident on the surface of the particles, electrons in the valence band are excited to jump into the conduction band and leave holes in the valence band. Therefore, an increase of anodic current is observed. In this particular case, the sulfide ions in solution may act as the hole acceptors, which scavenge the holes in the valence band and thereby being oxidized to elemental sulfur or sulfate (Figure 3a). On the other hand, if hole acceptors are not present in the solution (Figure 3b), the holes in the valence band may react with the lattice atoms, and the following overall oxidation reactions may occur:

In this case, pyrite dissolution rate will be proportional to the photocurrent observed on the inert electrode, and will be proportional to the light intensity. The rate of pyrite dissolution

can be determined by measuring the concentration of iron ions in solution as a function of time.

Polarization Experiments

Figure 4 shows the results of polarization experiments under the conditions of 1 M HNO_3 with and without 70 mg FeS_2 particles in solutions. It can be seen that anodic current increases dramatically in the presence of pyrite under illumination, as the potential of the inert electrode increases positively. The behavior of pyrite dissolution is dependent on the energetics of pyrite and the potential of the electrode. As shown in Figure 5a, when the potential applied is lower than E_c , the electrons will be injected into the conduction band, then transferred to the valence band, where pyrite is reduced. In this case, the pyrite will be dissolved cathodically. When the potential is higher than E_c (Fig. 5b), the electrode will accept the electrons in the conduction band, and the holes in the valence band will oxidize the lattice atoms. In this situation, illumination, which creates electrons and holes, can increase the anodic current on the inert electrode and can also increase the dissolution rate of the solid.

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FIGURE 1. Setup for (photo)electrochemical measurements.

FIGURE 2. Results of photocurrent measurements.

FIGURE 3. Illustration of photocurrent collection experiments in the presence (a) and absence (b) of the hole acceptors.

FIGURE 4. Results of polarization measurements.

(a)

(b)

FIGURE 5. Illustration of polarization experiments, where the potential of the electrode is lower (a), and higher (b) than E_c .

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