

Electrochemical Study of the Oxidation Products of FeS₂ Electrodes: The Formation of Fe(OH)₃

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Foi investigada a formação de Fe(OH)₃ sobre três minerais de FeS₂, usado como eletrodo, mediante medidas de potencial a circuito aberto e ensaios potenciodinâmicos em meio ácido (pH = 4,5). As amostras possuíam estruturas cristalinas e purezas diferentes. Constatou-se que o filme, inicialmente, formado durante o polimento é dependente da estrutura cristalina. Quando se oxida a superfície das amostras por meio de uma varredura anódica a quantidade de Fe(OH)₃ formado depende, principalmente, do potencial de inversão e da pureza das amostras.

The formation of Fe(OH)₃ on three FeS₂ minerals, used as electrodes in acid medium (pH = 4.5), was investigated employing open circuit potentials and potentiodynamic measurements. Samples of different crystal structures and purities were studied. The surface film formed during the polishing of the sample depends on the crystal structure. The amount of Fe(OH)₃ produced during an anodic potential sweep is a function mainly of the potential at which the scan is reversed and of the purity of the sample.

Key words: iron sulphide electrodes; iron hydroxide; surface films.

Introduction

Iron disulfide (FeS₂) appears in two crystalline structures: cubic for the pyrites and orthorhombic for marcasite. The majority of the published papers deals with pyrites. In the present communication the determination of the reduction charges of Fe(OH)₃, in acid medium and under potentiodynamic conditions is discussed for both the crystalline forms, pyrites and marcasite.

Experimental

Electrodes were prepared using two samples of pyrites and one of marcasite. The pyrites were of two different origins: igneous and metamorphic. Their purity was estimated determining the content of iron by means of volumetry (potassium dichromate). The electrical contacts were made with silver paste, and the samples were embedded in polyester resin. A reversible hydrogen electrode (RHE) was used as reference electrode, and the potentials were converted to the standard hydrogen electrode (SHE) scale, assuming (RHE - SHE) = 0.25 V. Thermodynamic data were taken from the literature¹, the concentration of the soluble species, Fe²⁺ and H₂S, was assumed to be equal to 10⁻³ M.

A solution 0.5 M CH₃COOH and 0.5 M CH₃COONa with pH = 4.5 was employed as electrolyte.

Before each experiment the electrode was polished with 600 emery paper and washed with distilled water. The electrode was introduced into the previously deaerated solution and, after one minute, the potential sweep carried out with a scan rate $v = 20 \text{ mV s}^{-1}$. The temperature was controlled at $(24 \pm 1) ^\circ\text{C}$.

Results and Discussion

The open circuit potentials were recorded after the electrode had been immersed in the solution for one minute. The values of E_{OC} increase with time and are higher for the

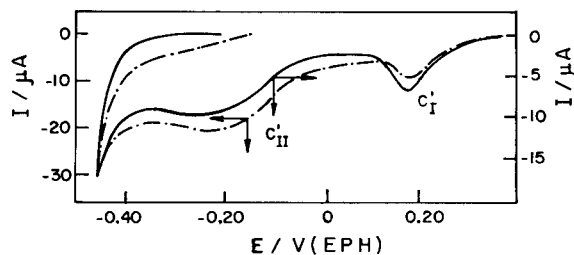


Figure 1. Cyclic voltammograms of igneous (---) and metamorphic (—) pyrite in acetic acid - acetate buffers, pH=4.5; $v = 20 \text{ mV s}^{-1}$; geometric areas: 14.1 mm^2 (igneous pyrite) and 4.7 mm^2 (metamorphic).

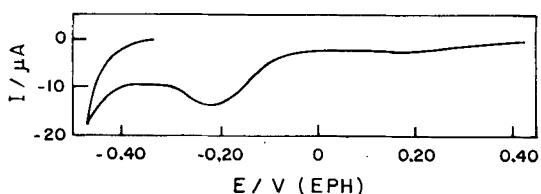


Figure 2. Potentiodynamic profile for marcasite in acetic acid-acetate buffers, $\text{pH}=4.5$; $\nu = 20 \text{ mV s}^{-1}$; geometric area of the electrode: 5.0 mm^2 .

marcasite than for pyrites ($E_{\text{OC}}[\text{marcasite}] = 0.45\text{-}0.50 \text{ V}$; $E_{\text{OC}}[\text{pyrites}] = 0.30\text{-}0.40 \text{ V}$). The difference between E_{OC} and the equilibrium potentials (0.33 and 0.35 V for $\text{Fe}^{2+}, \text{S}/\text{FeS}_2$ and $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$, respectively) increases with time. These potential differences suggest that a passivating film is developed².

During a potential sweep towards more negative potentials, two cathodic current peaks are observed, c_1' and c_{II}' (Figs. 1 and 2). Peak c_1' can be attributed to the reduction reaction of $\text{Fe}(\text{OH})_3$, since the potential at the beginning of the peak coincides with the potential of the $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ system.

The equilibrium potential of the $\text{FeS}_2/\text{FeS}, \text{H}_2\text{S}_{(\text{aq})}$ electrode is equal to -0.01 V . At this potential the current peak c_{II}' is initiated; therefore, it can be assumed that reduction of S_2^{2-} to FeS_2 occurs. Several authors verified that at more negative potentials the decomposition of pyrite becomes intense, with the simultaneous formation of H_2S and H_2 . At potentials near to c_{II}' , the reduction of S to H_2S is thermodynamically possible.

The potentiodynamic profiles shown in Figs. 1 and 2 remain unchanged if the solution is stirred during the potential sweep. This behavior is characteristic when interfacial species are reduced. Thus, it is confirmed that the reactants in that potential range are $\text{Fe}(\text{OH})_3$, FeS_2 and S .

Taking into account the probable processes which give origin to the current peaks c_1' and c_{II}' , it can be presumed that the film formation is initiated during polishing, and that marcasite is oxidized, forming less $\text{Fe}(\text{OH})_3$. On the other hand, the higher value of E_{OC} is due, possibly, to the higher

amount of sulphur formed, in comparison to the pyrites. This is understood considering that a film formed by sulphur has a more efficient protective action than that of iron hydroxide, which dissolves yielding $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^{2+}$; for high $\text{Fe}(\text{III})$ concentration the equilibrium is reversed favoring $\text{Fe}(\text{OH})_3$ precipitation⁵. Adsorption of $\text{Fe}(\text{III})$ species occurs simultaneously. The concentration of $\text{Fe}(\text{III})$ in solution varies, therefore, with time making impossible to isolate the influence of solubilization of the surface film on the potentiometric results.

A typical current-potential profile for the marcasite electrode at $\text{pH} 4.5$ is shown in Fig. 3A. The potentiodynamic profile recorded for marcasite is similar to that for pyrite (Fig. 3B). The comments for marcasite are therefore also valid for the pyrites.

During a potential sweep towards positive potentials, an anodic current that increases exponentially with potential is observed (Fig. 3). In that potential range, the oxidation of the FeS_2 surface yielding S , SO_4^{2-} and $\text{Fe}(\text{OH})_3$ is thermodynamically favoured. During the scan in the reverse direction, two cathodic current peaks are recorded. It was already seen

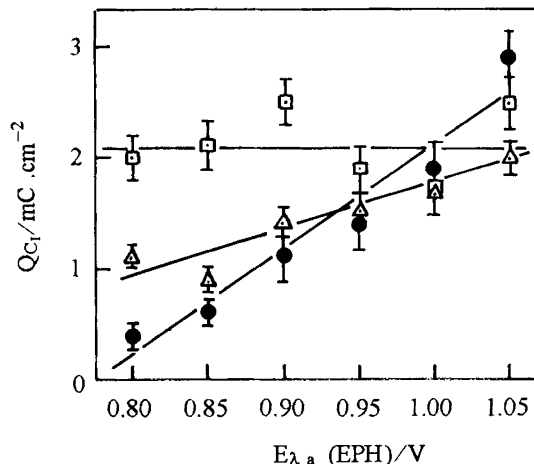


Figure 4. The variation of the reduction charges of $\text{Fe}(\text{OH})_3$ with the sweep reversion potential: (\square) igneous pyrite; (\bullet) metamorphic pyrite; (\triangle) marcasite.

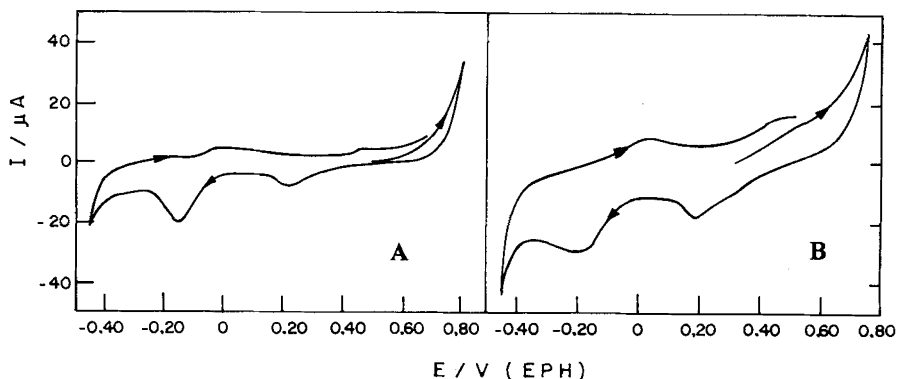


Figure 3. Voltammograms for FeS_2 electrodes in acetic acid-acetate buffers, $\text{pH}=4.5$; $\nu = 20 \text{ mV s}^{-1}$; (a) marcasite (geometric area: 5.0 mm^2), (b) igneous pyrite (geometric area: 14.7 mm^2).

that, at the first peak the reduction of Fe(OH)₃ occurs; the charge corresponding to peak c_I, at 0.05 V, is related to that reaction. The charge related to peak c_{II}, i.e., the reduction of the Fe(OH)₃ formed during polishing, must, however, be subtracted.

Figure 4 shows the charges corresponding to peak c_I, corrected taking into account E_{λa}. The metamorphic pyrite, with purity 99.4 %, exhibits a higher dependency of the Fe(OH)₃ formation on E_{λa}. The igneous pyrite, a sample more impure (purity 97.0 %), yields a relatively constant value of hydroxide at the investigated potentials. Therefore, the different behavior of the two samples is not due solely to the different crystal structures. Finally, it is observed that the formation of Fe(OH)₃ in the case of marcasite, 98.7 % pure, presents a behavior intermediate to those of the pyrites.

Acknowledgments

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