



Evaluation of the protective effect of polysiloxane coating on pyrite with electrochemical techniques

Ge-xin You^{a,*}, Chang-chun Yu^a, Yi Lu^a, Zhi Dang^b

^a School of Mechanical & Automotive Engineering, South China University of Technology, Guangzhou 510640, China

^b College of Environmental Science and Engineering, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

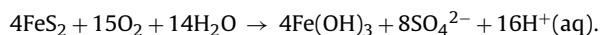
The efficiency of polysiloxane coating to suppress the pyrite oxidation under environmentally relevant conditions was investigated with electrochemical techniques. Cyclic voltammogram, Nyquist plot or Tafel test were performed in the conditions of different polysiloxane proportions in modifying agent, pH values, Fe³⁺ concentrations and volumes of water impact. The increased proportion of polysiloxane in the modifying agent would enhance the protective effect of the coating. The modifying agent with the least proportion of polysiloxane was used in subsequent experiments to illustrate the excellent passivation of polysiloxane. The results indicated that coating on the pyrite had good protective effect to resist the oxidation of pyrite in the aggressive condition of pH 2. Moreover, there were no distinctive differences in coated pyrite behaviors during anodic oxidation in solutions with different pH values. Furthermore, in a wide range of Fe³⁺ concentrations, the coating on the pyrite still showed good effect to retard the pyrite oxidation. Finally, the coating on the pyrite possessed good washing durability. Therefore, polysiloxane coating had great potential to develop a new AMD suppression strategy.

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1. Introduction

The pyrite is unstable in oxidizing environments. When exposed to oxygen and water during mining, pyrite can undergo rapid chemical weathering to produce acid mine drainage (AMD). The AMD contains abundant H⁺, Fe³⁺, SO₄²⁻ and heavy metal ions [1]. The heavy metal ions which cannot be removed by biological system will degrade soil and lead to withering, even death of ground vegetation [2,3]. Moreover, the AMD cause corrosion of mining equipment, threatening the safety of miners [4,5].

The production of AMD can be reduced by preventing the surface chemical reactions of pyrite, such as surface oxidation, surface dissolution and surface absorption [6]. Water and oxygen play important roles in the surface chemical reactions, shown as follows [7]:



A protective film formed on the pyrite surface, which prevent it from contacting water and oxygen, will greatly restrain the above reaction. Inorganic salts, such as phosphate [8–10], and organic complexes 8-hydroxyquinoline [11], triethylenetetramine

[12] have been applied to suppress surface chemical reactions on pyrite surface. Unfortunately, they have fatal disadvantages. For example, Phosphate may lead to water eutrophication and even accelerate pyrite's bio-oxidation [12]. 8-Hydroxyquinoline and triethylenetetramine are toxic to the environment.

Polysiloxane, a harmless and environmentally friendly material with low surface tension and excellent film-forming property [13], has been widely used in many fields, especially in construction [14]. However, knowledge on the application of polysiloxane for controlling AMD is scarce. The protective effect of polysiloxane on pyrite has been evaluated with chemical method [15]. In addition, most of the protection effect of coatings on pyrite was evaluated by chemical method [9–12]. However, very little studies are available on the evaluation of polysiloxane coating passivation on pyrite with electrochemical methods. This work was going to study the electrochemical behaviors of pyrite coated with polysiloxane.

2. Experimental

2.1. Materials and material processing

The pyrite sample in the experiments was obtained from Yunfu city Warner new material science and technology Company. PTFE (polytetrafluoroethylene) latex was got from Guangzhou Xingshengjie Science and Technology Company, China. Its density,

* Corresponding author. Tel.: +86 13929586358.

E-mail addresses: gxyou@scut.edu.cn (G.-x. You), yuchangchun521@126.com (C.-c. Yu), chzdang@scut.edu.cn (Z. Dang).

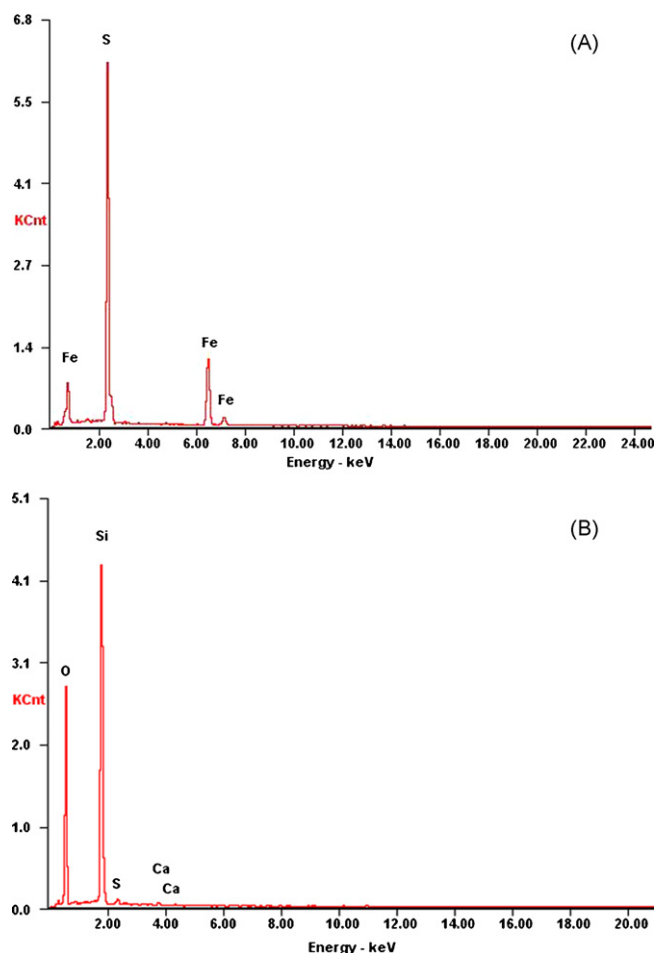


Fig. 1. SPM images of pyrite.

Table 1
Element contents in the pure sample area (%).

Element	Mass percentage	Atomic percentage
S	54.23	67.36
Fe	45.77	32.64

viscosity and pH were 1.50–1.55 g/cm³ at 20 °C, 6–15 mm²/s at 30 °C and 9, respectively.

The pyrite powder were ground with an agate mortar and screened to the particles with the size less than 75 μm. 0.2 mL PTFE latex and 1 g pyrite powder were evenly mixed, and then the mixture was orderly processed with the mold and a Tablet Pressing Machine to product slice whose diameter and the thickness were 16 mm and 0.6 mm, respectively. The slices were stored in an ainer.

The pyrite powder was tested with scanning probe microscopy (SPM). Its images were shown in Fig. 1 and its compositions were listed in Tables 1 and 2.

Table 2
Element contents in the impurity area (%).

Element	Mass percentage	Atomic percentage
O	51.47	65.21
Si	46.84	33.80
S	01.01	00.64
Ca	00.68	00.34

2.2. The preparation of modifying agent and electrolyte solution

The modifying agent was prepared through homogeneous mix of tasteless kerosene, 10 g of hydrogen polysiloxane, 0.3 g teraethoxysilane and 0.15 g dibutyltin dilaurate.

Electrolyte solution was 0.2 M (moles per liter) sodium sulfate solution, which was prepared with anhydrous sodium sulfate and de-ionized water.

All solution used in the experiment were prepared with concentrated analytical grade reagents, diluted with distilled water.

2.3. Treatment of polysiloxane coating on pyrite

The pyrite slices prepared previously were immersed in the modifying agent for 1 h, then dried and solidified for 24 h at room temperature.

2.4. Testing equipment and testing parameter setting

The electrochemical properties of the uncoated and coated pyrite with agent were measured with a Reference 600 potentiostat equipped from American Gamry Instruments.

A three-electrode cell was employed for the electrochemical measurements. The cell was full of the measured electrolyte solution with an effective volume of 130 mL. The saturated calomel electrode was used as the reference electrode with a Luggin–Haber capillary-tip to the surface of working electrode, a preformed pyrite slice [2.00 square centimeters (cm²), the working area 0.95 cm²]. A piece of platinum (15 mm × 15 mm) in its own compartment was used as counter electrode.

Cyclic voltammogram tests were conducted in configured electrolytes at scan rate of 20 mV/s. The scan range was from –1.2 V to +1.2 V. Three cycles were scanned for each voltametric test and the second cycle was reported as the cyclic voltammogram.

The electrochemical impedance spectroscopy (EIS) tests conditions were set as follows: (a) sweep range: 10⁵ to 0.1 Hz; (b) sweep points: 20; (c) the AC signal amplitude: 15 mV sine wave; (d) research area: 0.95 cm².

The polarization curve test was carried out from –200 mV to +200 mV vs. open circuit potential, at a rate of 1 mV/s.

3. Results and discussion

3.1. Surface characterization of polysiloxane coating on pyrite

The surface chemical composition of coated pyrite, uncoated pyrite and polysiloxane were characterized by Raman spectroscopy. The results were showed in Fig. 2.

Compared with spectrum of pure polysiloxane in Fig. 2, the standard spectra of PTFE, Fe₂O₃·nFeO, Raman peaks on the coated and uncoated pyrites in Fig. 2 were attributed in Table 3.

The peaks of 2172, 2907 and 2970 cm⁻¹ in Raman spectrum of the coated pyrite could be clearly assigned to polysiloxane, which confirmed that a polysiloxane film was formed on the pyrite surface.

The Raman spectra of coated pyrite (Fig. 3a) after electrochemical test, uncoated pyrite after (Fig. 3b) and before (Fig. 3c) the test in the range from 200 to 800 cm⁻¹ showed the variations of compounds and their levels on the pyrite surface before and after the test.

The peak at 386 cm⁻¹ could be attributed to Fe₂O₃·nFeO and PTFE. The peak at 734 cm⁻¹ was only assigned to PTFE. The change of the intensity ratio between 386 and 734 cm⁻¹ could be used to express the Fe₂O₃·nFeO level on the pyrite surface. The approximate intensities and ratios between 386 and 743 cm⁻¹ were listed in Table 4.

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