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Voltammetric investigation on iron-(nickel-)sulfur surface under conditions for the emergence of life

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E-mail: thiago.altair.ferreira@usp.br, douglas.galante@lnls.br and hamiltonvarela@usp.br**Keywords:** emergence of life, cyclic voltammetry, hydrothermal systems, mackinawite

Abstract

Iron (II) sulfide minerals have gained attention in the last decades due to their relevance in hypotheses for the emergence of life on the early Earth around 4 billion years ago. In the submarine vent theory, it has been proposed that those minerals, especially mackinawite, had a key role in prebiotic processes. Those are estimated to be present in a natural electrochemical setting, analogous to a chemiosmotic one, formed in the interface between the early ocean and the interior of the alkaline hydrothermal systems, the early vent-ocean interface. To evaluate this and other hypotheses, voltammetric studies were performed to better understand the electrochemical behavior of minerals under conditions analogous to the vent-ocean interface. The preliminary results presented here indicate that, in the potential range estimated to exist in that interface, mackinawite can transition to other mineral phases and may possibly coexist with other minerals, resulting from its oxidation. This can create a local chemical diversity. In addition, it has been tested a protocol for Ni incorporation in mackinawite structure, resulting in a surface that showed an interesting behavior in the presence of CO₂, although definitive experiments showed necessary for a deeper comprehension of that behavior. Overall, the results are consistent with previous results on electrocatalytical properties of Fe-Ni-S materials for CO₂ reduction, and also could lead to the emergence of a protometabolism on early Earth.

1. Introduction

The number of works investigating properties of iron (II) sulfides (FeS) using electrochemical techniques has increased. Their motivations were mainly from the fact that those compounds are products of surface corrosion of steel due to exposure to aqueous hydrogen sulfide [1–5], and are also ubiquitous in anoxic aqueous environment. Moreover, in the last decades, FeS minerals have gained attention due to their key roles in some hypotheses for the origin of life, such as the ‘Iron sulfur world’ and the ‘submarine vent theory’ (SVT) or ‘alkaline vent theory’ (AHV) [6–9]. In these hypotheses, FeS-based minerals were proposed to have a significant evolutionary relevance for life as potential protoenzymes due to their catalytic properties.

Among all FeS phases, mackinawite (FeS_m) has been reported as the most soluble stable one and whose formation kinetics is faster compared to other stable phases [3]. In addition, there are some relevant questions regarding electrochemical properties of FeS minerals, especially mackinawite, which still need answers. Their sensitivity to pH and redox conditions [10] and their reactivity to oxygen [11] difficult the performing of experiments under room conditions. Therefore, *in situ* methods, such as those commonly used in electrochemistry, are more adequate to be applied.

This publication presents data from voltammetric studies using *in situ*-synthesized FeS films as working electrodes, under conditions analogous to an early ocean-hydrothermal-vent interface. Here, it is presented a protocol for a rigorous investigation of electrochemical properties of metastable mackinawite surface under conditions of the interface between alkaline hydrothermal vents and the ocean in the early Earth, 4 billions of

years ago. Moreover, we investigate the incorporation of Ni in mackinawite mineral and its effects in the same conditions. The major aim is to provide experimental background to discuss the SVT hypothesis for the emergence of life.

2. Methods

2.1. Materials and solutions preparation

All solutions were prepared with high purity water (Milli-Q system, Millipore, 18.2 M Ω .cm) and with reagent grade chemicals. For the preparation of electrolytes, it was used 0.1 mol.l⁻¹ sodium phosphates to keep them buffered during the experiments. Na₂HPO₄.6H₂O (Mallinckrodt Baker, 99.8%) was used for pH 11, NaH₂PO₄.H₂O (J T Baker) for pH 7, and Na₂HPO₄/NaH₂PO₄ for pH 5.5. For testing the electrochemically induced Ni incorporation to FeS, a 0.01 mol.l⁻¹ Ni²⁺ solution was prepared dissolving NiCl₂.6H₂O (Synth, 98%). All electrolytes used were deoxygenated by bubbling argon (White Martins, 99,998%) previously to the experiments for at least 1 h and the gas is kept flowing in near-atmospheric pressure during the measurements. For CO₂-saturated solutions, CO₂ gas (Linde, 99,99%) is also bubbled for at least 1 h previously to the experiments and is kept flowing in near-atmospheric pressure during them.

2.2. Electrode preparation and electrochemical setup

Experiments were performed using a 50 ml three-electrode glass cell. The working electrode was a FeS film electrodeposited over an AISI 1070 steel surface disc set at the bottom of the cell. This steel disc was fixed with a single side faced up in a Teflon holder and the surface in contact with the electrolyte was of 0.785 cm². The reference electrode was an AgCl-coated Ag wire immersed in a compartment with a glass frit and filled with a KCl saturated solution (referred as Ag/AgCl sat.d electrode) and this compartment was immersed in a glass luggin. Hence, the counter electrode was Pt flag with sufficiently high surface area.

Prior to each experiment, the steel disc surface was prepared and the FeS film was electrodeposited. The steel disc was etched in concentrated HCl for about 1 min and thoroughly rinsed in high purity water. Then, it was polished with SiC papers (300 and 1200 grit), washed successively with water, acetone and then it was electrochemically cleaned. This last step consisted in cathodically polarizing (*ca.* -2.0 V versus Ag/AgCl sat.d) for around 1 min in a water solution, creating a stream of H₂.

The FeS film was formed electrochemically in a three-electrode glass cell with two compartments separated by a fine glass frit. The method was based on results from Shoesmith *et al* 1978 [2] and Xiaoran, 2006 [12]. In this cell, the counter electrode was separated from the other two electrodes. Then FeS was produced polarizing the steel disc electrode at -0.3 V (versus Ag/AgCl sat.d) for around 1 min at a pH 10, 0.05 mol.l⁻¹ Na₂S (Êxodo científica, 99.5%) + 0.05 mol.l⁻¹ NaCl (Panreac, 99.5%). Then, the excess of precipitated was removed using water and the electrode was quickly transferred to the cell at which the results were produced.

In the tests for the electrochemically induced Ni incorporation to FeS, the film was immersed in a 0.01 mol.l⁻¹ NiCl₂, deoxygenated solution for 10 min in a fixed potential that showed as stable after a few seconds of open circuit potential (OCP). Then, the surface was rinsed in water and quickly transferred to a deoxygenated buffered solution for voltammetric studies. The cyclic voltammetries (CVs) obtained for FeS films were performed after this surface was kept in OCP in the buffered solution for 10 min.

3. Results

In figure 1(a), it is shown the resulting reproducibility of the protocol tested to investigate the metastable FeS surface. Moreover, figure 1(b) emphasizes the peaks observed in the CV for FeS recorded in pH 7. Based on the literature and on the thermodynamic information in Pourbaix diagrams [1, 13–16], four potential regions are identified between -0.4 to 0 V (versus RHE). Based on Eh:pH diagrams [17], region 1 may be attributed to the transition from FeS to Fe₇S₈. In region 2 (*ca.* -0.1 V), the increasing of the current is associated to the dissolution of Fe²⁺. Region 3 (*ca.* -0.05 V) is attributed to the formation of Fe³⁺-oxide (γ -Fe₂O₃) [14]; however, it is expected that there is also a competition between the iron [III] oxide formation and its destruction while reacting with sulfide, leading to an increasing of the current on higher potentials. Finally, region 4 is attributed to the FeS reduction to Fe⁰. At potentials lower than those of region 4, a cathodic tail-like region must be a result from the H₂ formation, ohmic drop and possible other phenomena accordingly to each medium. However, these assignments are tentative and experimental investigation are under process for comparison with those made in e.g. (1, 15, and 16).

Figure 2 illustrates the resulting CVs and current densities for potential steps for FeS as working electrode under different pH condition and after the exposure of the FeS to Ni²⁺. Potential steps techniques are commonly used for suppressing background current due to capacitive effects in the solution-electrode interface. Therefore,

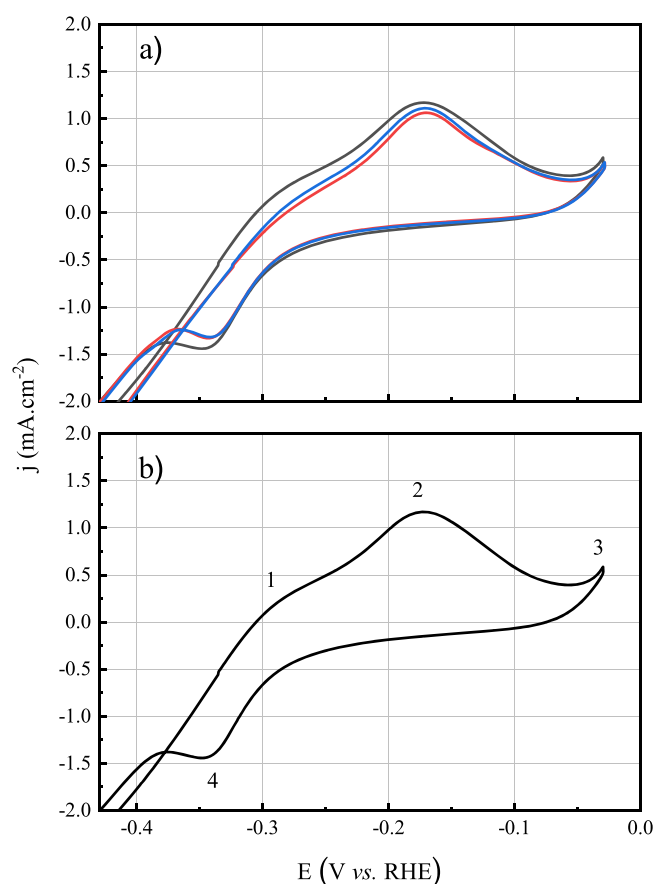


Figure 1. Cyclic voltammeteries of FeS surface at 10 mV.s^{-1} on pH 7.0.1 mol.l⁻¹ sodium phosphate buffer at room temperature and pressure. (a) Illustration on the reproducibility of the setup and protocol tested; (b) Highlight the peaks and shoulders resulting from phase transitions of the surface and other phenomena.

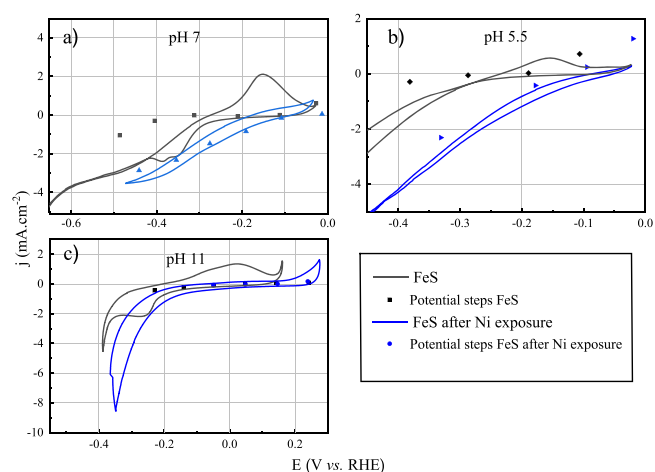


Figure 2. Cyclic voltammeteries at 10 mV.s^{-1} under room temperature on pHs: (a) 7; (b) 5.5 and (c) 11. There are presented the voltammogram for FeS as working electrode after OCP for 10 min in Ni-absent buffered solution (black lines) and in 0.01 M Ni^{2+} (blue lines). There are also presented results for potential steps applied for FeS as working electrode after OCP for 10 min in Ni-absent buffered solution (black dots) and in 0.01 M Ni^{2+} (blue dots).

currents detected using this technique are due predominantly to charge transfer in that interface. Using the regions presented in figure 1(b) as reference, it is detected the same anodic transitions, despite the different current intensities. Notwithstanding, the cathodic peak observed in the region 4 is not observed on pH 5.5, probably due to an overlapping of peaks. Moreover, it is noteworthy that CVs, after FeS exposure to Ni²⁺ (blue

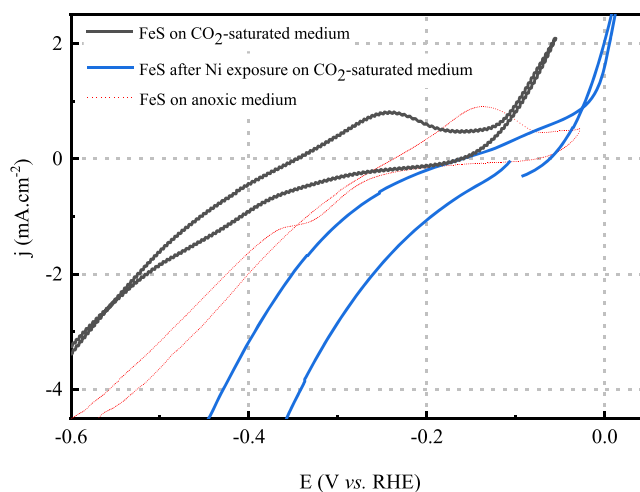


Figure 3. Cyclic voltammeteries at $10 \text{ mV} \cdot \text{s}^{-1}$ for FeS; after OCP for 10 min in Ni-absent pH 5.5 buffered solution (black line) and Ni-rich solution (blue line). Voltammeteries were performed in CO_2 -saturated, pH 5.5 buffered solution. As reference, it is also showed a CV of FeS under anoxic only, pH 5.5 buffered solution (red dashed line).

lines), show no anodic peaks or shoulders clearly observed compared to results of FeS without exposure to the ion (black lines).

Figure 3 shows the results when CVs were performed under an anoxic, CO_2 -saturated, pH 5.5 aqueous medium (black and blue lines) compared to CV obtained on the same pH, under anoxic-only conditions (red dashed line). There is a very small difference in the current intensity of transitions under anodic currents comparing the voltammograms under anoxic-only and CO_2 -saturated conditions without Ni. However, there is a difference at lower potential regions, indicating that CO_2 results in a current inhibition effect on FeS surface. On the other hand, in this same region, there is a considerable current enhancing after Ni is incorporated to FeS. This result indicates that can be an electron charge transfer from the surface to the soluble CO_2 although H_2 formation must also be considered. These results corroborate previous works demonstrating that CO_2 reduction can be catalyzed by Fe-Ni-S minerals, besides its low efficiency compared to other surfaces [18–20].

4. Discussion

Mackinawite (FeS_m) is considered a key mineral in the SVT model for the emergence of life [6]. In this model, it is proposed that the seed for the process of emergence of life is situated in alkaline hydrothermal systems in the early Earth. The interface between the early ocean and the hydrothermal fluid, mediated by a carbonate barriers containing FeS and Fe-Ni-S, is estimated to produce natural electrochemical potentials (estimated from 0.2 to 1.4 V) [6, 21]. In this early vent-ocean interface, the mineral may had worked as an active site induced by the natural potentials forming an analogous setting to the chemiosmotic mechanism, universal in modern cells. Thus, In this work, the voltammeteries were performed under pH and potential conditions analogous to models of the mentioned interface.

Our results lead us to conclusions that FeS may have coexisted with other phases in the vent-ocean interface. This could result in a combination of interactions that each phase would develop which may contribute to the emergence of life or not.

Finally, Ni was showed to be incorporated to the FeS structure, probably resulting in a type of Ni-bearing mackinawite [22]. This incorporation were showed for another experimental context, resulting in stabilization of the mackinawite [23]. Moreover, the presence of Ni has showed evidences of enhancing catalytic activity of Fe-S surfaces, already reported in the literature [17].

5. Conclusions

Based on the reported results, it is concluded that the protocol developed to electrochemically investigate metastable FeS structures and Ni incorporation showed to be adequate, producing reproducible results.

In conclusion, the results presented point to important questions regarding the nature of the phases and the transitions that are feasible to occur on the interfaces described in the SVT. We expect that supplementary techniques and results will be performed to provide more background for the discussions opened here.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Conflicts of interest

The authors declare no conflict of interest.

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