

Voltammetry of Solid Microparticles of Some Common Iron- and Copper-Iron Sulfide Minerals

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Received: 2 September 2021 / Accepted: 21 January 2022 / Published: 2 February 2022

The electrochemistry of three common iron-sulfide minerals, i.e., pyrite (FeS₂), marcasite (FeS₂) and chalcopyrite (CuFeS₂), has been studied by voltammetry of solid microparticles for the purpose of obtaining typical voltammetric fingerprints for qualitative characterization and differentiation of mineral samples. Voltammetric patterns obtained under conditions of conventional cyclic voltammetry reflect the complex electrochemistry of the studied minerals, which have been immobilized on the surface of paraffin-impregnated graphite electrodes in the form of randomly distributed microparticles in contact with aqueous electrolytes. Voltammetric features depend strongly on the methodology of the cyclic voltammetry experiment, which can be conducted either by conditioning of the modified electrode at a given potential prior to the voltammetric scan or by commencing the voltammetry experiment from the open circuit potential. Highly structured, reproducible, specific, and self-normalized voltammetric patterns can be obtained under conditions of fast and sensitive square-wave voltammetry, which enables clear differentiation between the studied minerals, demonstrating that square-wave voltammetry can be used as a technique for in situ, fast and simple qualitative mineral characterization.

Keywords: iron-sulfide minerals, solid microparticles, voltammetric fingerprints, cyclic voltammetry, square-wave voltammetry

1. INTRODUCTION

The methodology for characterization of solids by means of conventional electrochemical techniques, e.g., chronoamperometry and voltammetry, was developed decades ago [1], as the electrochemistry of solid materials is far more challenging than conventional solution electrochemistry. In very early studies, the solid phase to be studied was the working electrode itself

[2], which is applicable to electrically conducting or semiconducting solids. The method has several drawbacks in terms of low reproducibility (the surface of the electrode changes over the course of the experiment) and insufficient voltammetric resolution (the whole electrode produces high currents). Later, the solid material was dispersed in a carbon paste or other carbon materials to prepare the working electrode [3], which is an effective yet time-consuming procedure. A step forwards has been done by introducing voltammetry of solid microparticles (initially termed abrasive stripping voltammetry) [4], which has overcome most of the previous drawbacks. Voltammetry of solid microparticles is a simple and efficient experimental methodology based on the mechanical immobilization of solid particles (in a quantity of micrograms) on the soft surface of paraffin-impregnated graphite electrodes (PIGEs). The method has found a plethora of applications, ranging from archaeometry [5,6] to the study of immobilized microdroplets [7] and vesicles [8]. When solid microparticles are concerned, the methodology has been used for analysing chemical composition [9], purity [10], chemical stability [11], kinetics of electrochemical and chemical reactions [12], and electrosynthesis [13, 14]. Moreover, experimental data collected under voltammetric conditions can be informative on the structure of the solids [15]. The overall methodology is elaborated in detail in a specialized monograph [16].

The initial idea of abrasive stripping voltammetry was to electrochemically study the structure and chemical properties of minerals [17, 18]. The technique is especially suitable for on-site qualitative analysis of minerals, as electrochemical techniques can be applied in situ [19]. Considering that the required electrochemical instrumentation is cheap and portable, the overall electrochemical methodology is attributed to important advantages over conventional methods for mineral characterization (e.g., X-ray diffraction, mass spectrometry, bench-top IR spectroscopy or scanning electron microscopy coupled with energy dispersive spectroscopy). Moreover, electrochemical data collected under voltammetric conditions can be considered a sort of electrochemical spectrum, which is unique for a given mineral and specific experimental conditions.

Concerning the electrochemical techniques applied, differential pulse and cyclic voltammetry were often used as working techniques in the voltammetry of solid microparticles of minerals in early studies [17]. Since then, many other voltammetric, chronoamperometric and coulometric techniques have also been utilized [20]. Depending on the mineral, under voltammetric conditions, the potential can be applied in either the oxidative or reductive direction, starting from the open-circuit potential of the PIGE/mineral/electrolyte system. Because of the high electrochemical and chemical stability of minerals, such an approach frequently does not result in a well-developed voltammetric profile that can be used for qualitative analysis. For that reason, preliminary electrochemical reduction is recommended, commonly done by conditioning the modified electrode at a sufficiently negative potential (e.g., at -2.00 V vs. Ag/AgCl) for a certain period of time until all mineral particles are electrochemically reduced to the corresponding elementary metals. Following the conditioning step, the resulting metal particles are subject to electrochemical oxidation in the course of subsequent anodic potential scans. The latter method is very efficient for qualitative analysis of minerals that are composed of different metals, while the main drawback is that most of the immobilized solid mineral particles are virtually completely destroyed on the electrode surface prior to the experiment, and information on the structure and reactivity of the original mineral are lost. For these reasons, minerals

with similar chemical compositions but different structures cannot easily be voltammetrically differentiated [17].

The voltammetric outcome of the studied mineral depends significantly on the supporting electrolyte used in the course of the voltammetric experiment [21]. As inferred from Pourbaix diagrams [22], most minerals have many stable species in a neutral (or close to neutral) medium, resulting in very complex voltammetric profiles. Hence, a strong acid or alkaline medium was frequently used to make the electrochemistry as simple as possible. Additionally, well-defined voltammetric profiles have been obtained by removing the dissolved oxygen from the electrolyte solution [17]. However, intending to use voltammetry of solid microparticles for in situ mineral characterization, the voltammetric profiles in the presence of oxygen have to be analysed as well.

Many minerals have already been analysed with voltammetry of solid microparticles. Examples are copper- and iron-containing minerals: chalcopyrite (CuFeS_2), chalcostibite (CuSbS_2), cuprite (Cu_2O), and pyrite (FeS_2) [19]; thallium-containing minerals: $\text{Tl}_2\text{As}_2\text{SnS}_6$, Tl_2SnS_3 , $\text{Tl}_2\text{Sn}_2\text{S}_3$, Tl_4SnS_4 ; lead-antimony-containing minerals: zinkenite ($\text{Pb}_9\text{Sb}_{22}\text{S}_{42}$), plagionite ($\text{Pb}_5\text{Sb}_8\text{S}_{17}$), boulangerite ($\text{Pb}_5\text{Sb}_4\text{S}_{11}$) and many others [23, 24]. In the present communication, we report the qualitative identification of three minerals from North Macedonia by means of voltammetry of solid microparticles: pyrite (FeS_2), marcasite (FeS_2) and chalcopyrite (CuFeS_2). To the best of our knowledge, electrochemical data of marcasite (FeS_2) under voltammetry conditions of solid microparticles have not been reported thus far. The presented electrochemical study was conducted by means of conventional cyclic voltammetry (CV) and square-wave voltammetry (SWV), the latter being one of the most sensitive voltammetric techniques, enabling both mechanistic and kinetic characterization of electrode processes [25]. The general aim of the study is to provide typical voltammetric profiles to be used as electrochemical fingerprints for simple in-situ qualitative characterization of the studied minerals. This approach could also be beneficial to substitute for the common qualitative FTIR fingerprint analysis of these minerals, particularly because the sulfides absorb in the far-IR region and many laboratories are not equipped with such detectors.

2. EXPERIMENTAL

2.1. Samples

All mineral samples originate from North Macedonian mines. Pyrite was collected from the Bučim Mine, and marcasite was obtained from the Allchar Mine. Two different samples of chalcopyrite, designated chalcopyrite_1 and chalcopyrite_2, were obtained from Bučim and Sasa, respectively. The samples were selected, picked up from the ore under an optical microscope and fine-powdered for the electrochemical measurements, whereas single crystals were used for determination of the purity by means of X-ray microprobe analysis.

2.2. Electrochemical setup

Electrochemical study was performed with an electrochemical measuring station $\mu\text{Autolab}$ (potentiostat/galvanostat), model III, controlled by GPES computer software. The general procedure for

recording voltammograms under conditions of voltammetry of solid microparticles was identical to the procedure described elsewhere [16]. The three-electrode configuration consisted of PIGE as the working electrode, Ag/AgCl (3 mol/dm³ KCl) as a reference, and a graphite bar as the counter electrode.

All chemicals used were of analytical grade purity (Sigma-Aldrich). All solutions were prepared with purified water obtained from an Arium® Mini Plus purification system from Sartorius. An aqueous solution of KNO₃ at a concentration of 0.1 mol/dm³ was used as a supporting electrolyte.

2.3. X-ray microprobe analysis

The chemical composition of the individual minerals was determined by X-ray microprobe analysis using a JEOL-JSM 35-CF instrument and an EDX-TRACOR NORTHERN TN-2000 system. The mineral crystals were previously covered with a carbon layer with a thickness of 30 nm in a vacuum evaporator (JEOL JEE-4X). The accelerating voltage was set to 15 kV, the current power was adjusted to 15 mA, and the counting time was set to six seconds. The results represent the average values determined at three separate points from the conventional centre and periphery. The analyses were carried out at one point (1 µm) so that mechanical microinclusions could be avoided. The analytical scope of energy-dispersive X-ray spectroscopy (EDS) was from Na to U. All the elements up to Na were determined as a difference up to 100 wt %. Standards were used as follows: albite for Na; corundum for Al; barite for Ba; diopside for Mg, Si, Ca; biotite for K; chalcopyrite for S, Fe, Cu; pure substances Mo, Mn, Ti, Cd, Ag, Cr, Zr and stibnite for Sb. Sample chalcopyrite_2 has been reported to contain galena (PbS), whereas the remaining samples have shown extreme purity with only a negligible percentage of Cu in the pyrite specimen (Table 1).

Table 1. The results from an X-ray microprobe analysis of the studied minerals were compared to the ideal chemical composition (in wt%).

Element	Pyrite, FeS ₂ (Bučim)	Pyrite, FeS ₂ (theoretical)	Marcasite, FeS ₂ (Allchar)	Marcasite, FeS ₂ (theoretical)	Chalcopyrite_1, CuFeS ₂ (Bučim)	Chalcopyrite_2, CuFeS ₂ (Sasa)	Chalcopyrite, CuFeS ₂ (theoretical)
S	53.24	53.45	52.46	53.45	33.12	32.33	34.94
Fe	46.30	46.55	47.54	46.55	31.04	24.83	30.43
Cu	0.46	/	/	/	35.84	26.55	34.63
Co	<0.01	/	<0.01	/	<0.01	<0.01	/
Ni	<0.01	/	<0.01	/	<0.01	<0.01	/
As	<0.01	/	<0.01	/	<0.01	<0.01	/
Sb	<0.01	/	<0.01	/	<0.01	<0.01	/
Pb	<0.01	/	<0.01	/	<0.01	16.29	/

3. RESULTS AND DISCUSSION

The chemistry and electrochemistry of pyrite [26, 27, 28, 29, 30] and chalcopyrite [31, 32, 33] have been intensively studied. Electrochemical studies, including voltammetry, amperometry and potentiometry, are based predominantly on the experimental methodology where the studied mineral itself is the working electrode [2]. Our study commenced with inspection of the open circuit potential (OCP) of the PIGE-modified electrode in contact with the supporting electrolyte to inspect the chemical reactivity of the studied minerals (Fig. 1). The open circuit potential shifts to more negative values with time for all studied minerals, stabilizing after a certain time period, which depends on a particular mineral. The OCP shift is associated mainly with the surface phenomena of oxygen and water adsorption on the surface of immobilized solid mineral particles, in particular to the three-phase boundary junction where the PIGE, mineral particle and aqueous supporting electrolyte solution meet. More importantly, OCP variation agrees with the chemical reactivity of these minerals with water and dissolved oxygen to form ions and/or other oxidized species (depending on the pH) [34, 35]. As Fig. 1 shows, chalcopyrite is chemically more stable as the OCP value stabilizes at approximately 50 s, whereas pyrite and marcasite require longer than 100 s for chemical stabilization of the surface of their microparticles.

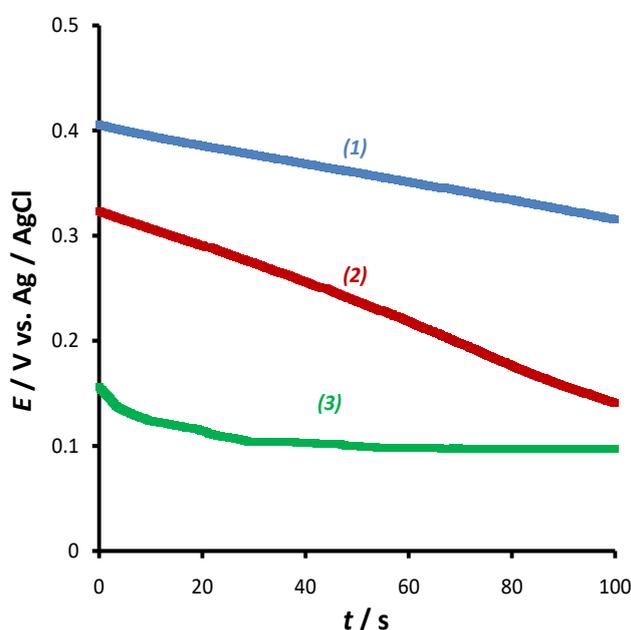


Figure 1. Open circuit potential of the PIGE electrode modified with solid particles of (1) pyrite (FeS_2), (2) marcasite (FeS_2) and (3) chalcopyrite (CuFeS_2) as a function of time in contact with a 0.1 mol/dm^3 aqueous solution of KNO_3 .

In the first set of voltammetric experiments, cyclic voltammetry was applied by previous conditioning of the modified electrode at a potential of -2.000 V (Fig. 2). As previously mentioned, the conditioning of the electrode at a very high negative potential aims to transform mineral particles to elemental metals and corresponding anions (i.e., sulfide ions). Thus, in the initial anodic potential scan of the cyclic voltammetry, anodic stripping peaks at -0.875 V (peak I) and -0.630 V (peak II) are

developed for all three minerals (Fig. 2), whereas chalcopyrite features an additional anodic stripping peak at approximately 0.00 V (peak III) (Fig. 2C and D).

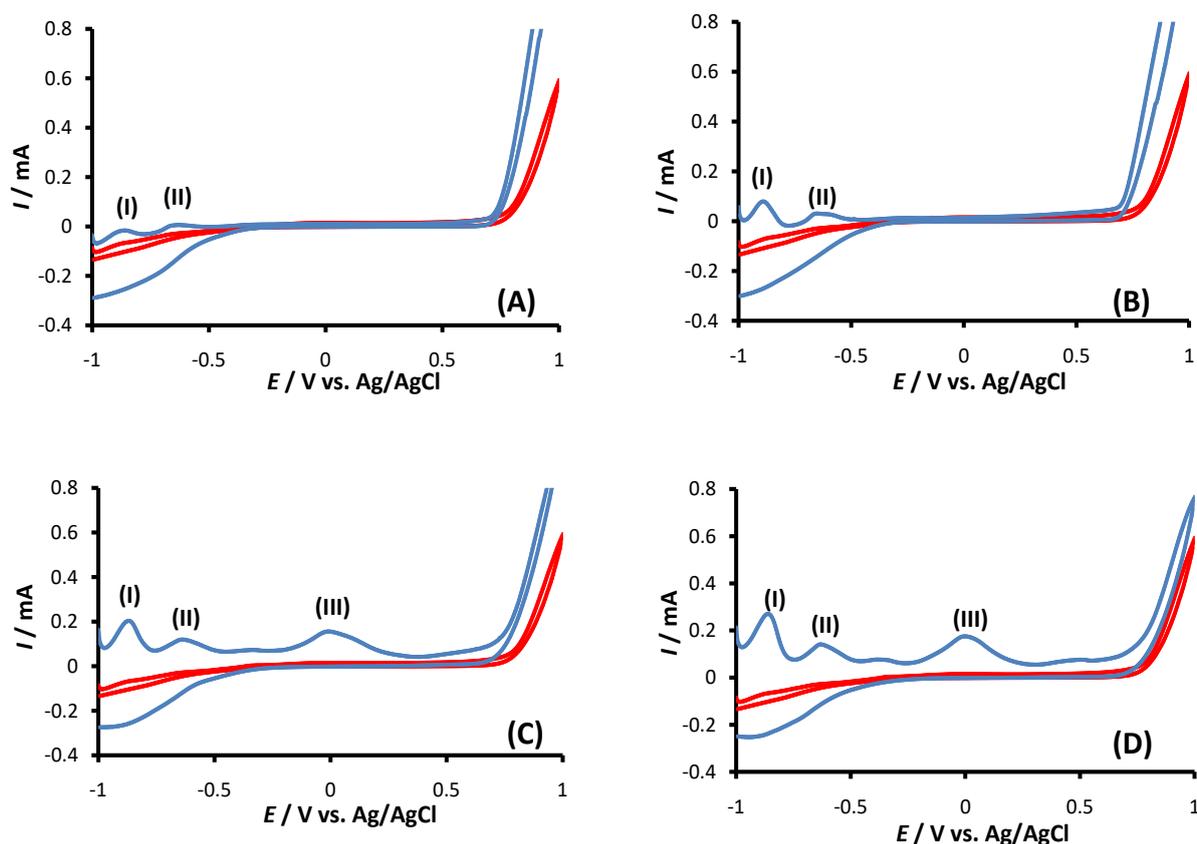
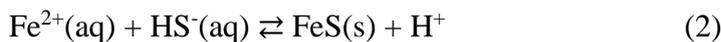


Figure 2. Typical cyclic voltammograms of (A) pyrite (FeS₂), (B) marcasite (FeS₂) and (C and D) chalcopyrite (CuFeS₂; sample _1 and sample _2, respectively) recorded following conditioning of the modified electrode at a potential of -2.000 V for 60 s. The initial potential of cyclic voltammograms is -1.000 V while the first vertex potential is 1.000 V, at the scan rate of $\nu = 50$ mV/s. The red curves correspond to the cyclic voltammetric response of the blank (i.e., unmodified PIGE electrode). Other conditions are same as in Fig. 1.

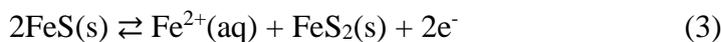
The first oxidation peak I is assigned to the anodic stripping process of elemental iron, which is formed during the conditioning step (reaction 1) [36]. In addition, it is plausible to assume that the conditioning step results in S²⁻ formation in the vicinity of the electrode surface, present mainly as HS⁻ ions. Due to concomitant water reduction at the free electrode surface during electrode conditioning, one should consider that the diffusion layer is becoming more basic than the bulk solution.



Hence, electrode reaction (1) is predictably coupled with follow-up chemical reaction (2) to form sparingly soluble FeS(s) on the electrode surface.



Thus, the second anodic peak (II) is ascribed to the oxidation of FeS to form a pyrite-like chemical from FeS₂ (i.e., oxidation of S²⁻ to S₂²⁻) (reaction 3) [26]. Clearly, the structure of electrochemically formed FeS₂ is not necessarily identical to either pyrite or marcasite.



For chalcopyrite, there is another well-developed anodic stripping peak at approximately 0.000 V, which is ascribed to the oxidation of elemental copper:



In addition, there are two peaks in the cyclic voltammograms of chalcopyrite at potentials of -0.375 V and 0.500 V, with a very low intensity and irreproducible character.

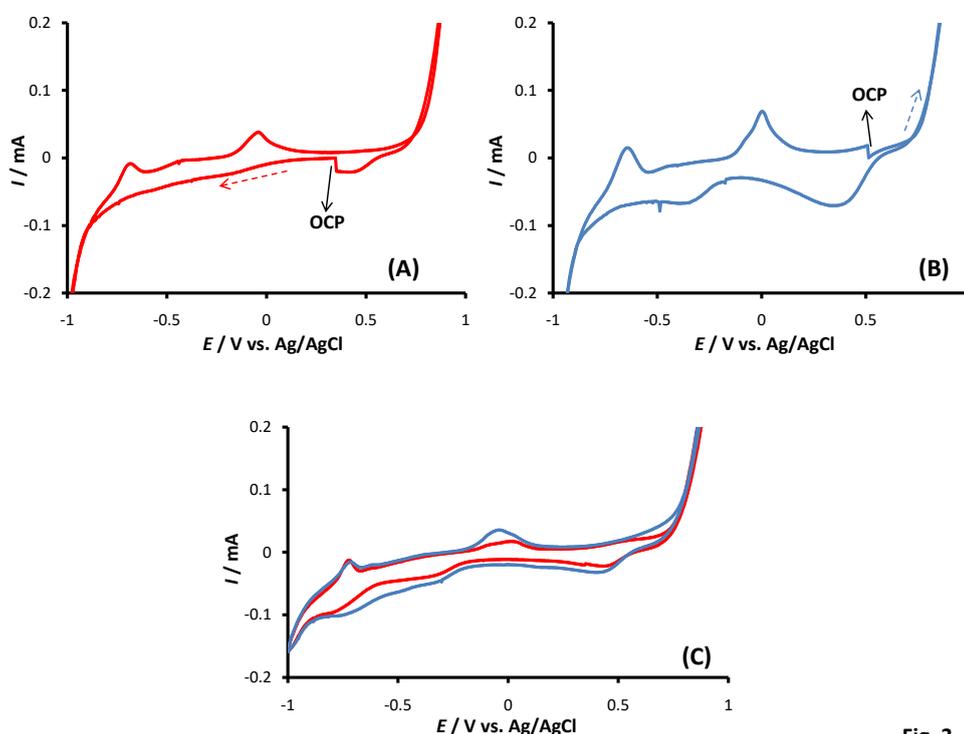


Fig. 3

Figure 3. Typical cyclic voltammograms of pyrite (FeS₂) recorded at scan rate $\nu = 50$ mV/s. **(A)** Starting from OCP, the potential was directed towards more negative values, with the first vertex potential of -1.000 V and the second vertex potential of 1.000 V. **(B)** Starting from OCP, the potential was directed towards more positive values, with the first vertex potential of 1.000 V and the second vertex potential of -1.000 V. **(C)** Typical cyclic voltammogram recorded from the OCP towards more positive values (**red line**) and towards more negative values (**blue line**) by repetitive potential cycling. The graph shows the third potential cycle of the corresponding cyclic voltammetry. Other conditions are same as in Fig. 1.

Rigorously speaking, electrode reactions (1-4) are more complex than described by the corresponding equation, considering that during conditioning of the electrode at -2.000 V, water and dissolved oxygen are concomitantly reduced, yielding mainly H_2O_2 , OH^- , gaseous H_2 and other reactive species. All these species affect the conditions in the vicinity of the electrode surface prior to the cyclic voltammetric experiment.

Following the conditioning steps, all minerals exhibit comparable catalytic activity on the positive potential side (i.e., at potentials higher than 0.800 V). In the last potential interval, $\text{FeS}_2(\text{s})$ is oxidized to Fe^{3+} (most likely in the form of $\text{Fe}(\text{OH})_3(\text{s})$) and $\text{SO}_4^{2-}(\text{aq})$, which are the most stable species with the highest oxidation state [22]. Obviously, voltammetric patterns of pyrite and marcasite are also identical due to identical chemical compositions of these structurally different minerals [37], as in the course of the conditioning step, both minerals are transformed into elemental $\text{Fe}(\text{s})$ and HS^- (aq) ions, which indeed are initial reactants for the forthcoming cyclic voltammetry.

To gain voltammetric patterns specific to each mineral, cyclic voltammetry was conducted starting from the OCP in both oxidative (towards 1.000 V) and reductive (towards -1.000 V) directions (Fig. 3). Cyclic voltammograms have different morphologies depending on the direction of the first scan (compare Panels A and B in Fig. 3), as exemplified with pyrite. Starting the voltammetric experiment from OCP towards more negative potentials (Fig. 3A), no reductive peaks are observed at $E > -0.900$ V. At more negative potentials, the limiting reduction current commences developing, which corresponds to the complete electrochemical reduction of the mineral to form $\text{Fe}(\text{s})$ and $\text{HS}^-(\text{aq})$. Thus, in the following anodic scan, typical peaks (I) and (II) emerge, likely corresponding to electrode reactions (1) and (3), respectively (Fig. 3A). When the experiment is conducted from OCP towards more positive potentials (Fig. 3B), a typical catalytic current in the form of an anodic current tail is seen at potentials more positive than 0.800 V, ascribed to the oxidation of the mineral to $\text{Fe}(\text{OH})_3(\text{s})$ and $\text{SO}_4^{2-}(\text{aq})$, as previously mentioned. Thus, in the following cathodic scan, two reduction peaks at approximately 0.400 V and -0.400 V can be observed, most likely related to the reduction of $\text{Fe}(\text{OH})_3(\text{s})$ species and other oxidation products of the mineral. After several repetitive potential cycles, the morphology of cyclic voltammograms becomes identical regardless of the direction of the potential vs. OCP. Thus, Fig. 3C can be considered a typical cyclic voltammogram of pyrite. Unfortunately, the morphology of the cyclic voltammograms of marcasite is not significantly different from the morphology of the cyclic voltammograms of pyrite, which precludes clear differentiation between two minerals based on cyclic voltammetry only. Thus, in the following text, we turn to the analysis of studied minerals with a more advanced voltammetric technique.

Considering the sensitivity, resolution and speed of voltammetric measurements, square-wave voltammetry (SWV) is a superior technique compared to CV [25]. Moreover, SWV provides insight into the mechanism of the electrode reaction comparable to CV, which altogether makes the technique an excellent tool for qualitative voltammetric screening of minerals. Typical SW voltammetric patterns are summarized in Fig. 4. Square-wave voltammetric experiments commencing from -1.000 V towards the anodic direction, at the frequency of potential cycles $f = 10$ Hz, with a height of potential pulses of 50 mV (i.e., SW amplitude $E_{\text{sw}} = 50$ mV) and a step of the underlying staircase potential of $\Delta E = 1$ mV. Starting the experiment from -1.000 V causes a partial reduction of the mineral particles to the previously mentioned products (e.g., $\text{Fe}(\text{s})$, $\text{HS}^-(\text{aq})$ for all three minerals, and $\text{Cu}(\text{s})$ for chalcopyrite).

However, unlike experiments conducted by conditioning of the modified electrode at -2.000 V in CV, reduction products in SWV coexist with the parent mineral particles on the electrode surface, providing a basis for rich chemical and electrochemical activity [38, 29]. Thus, the reaction mixture formed in the vicinity of the electrode surface at a starting potential of -1.000 V in SWV results in voltammetric profiles specific to each mineral, as depicted by the net SW voltammograms in Fig. 4A.

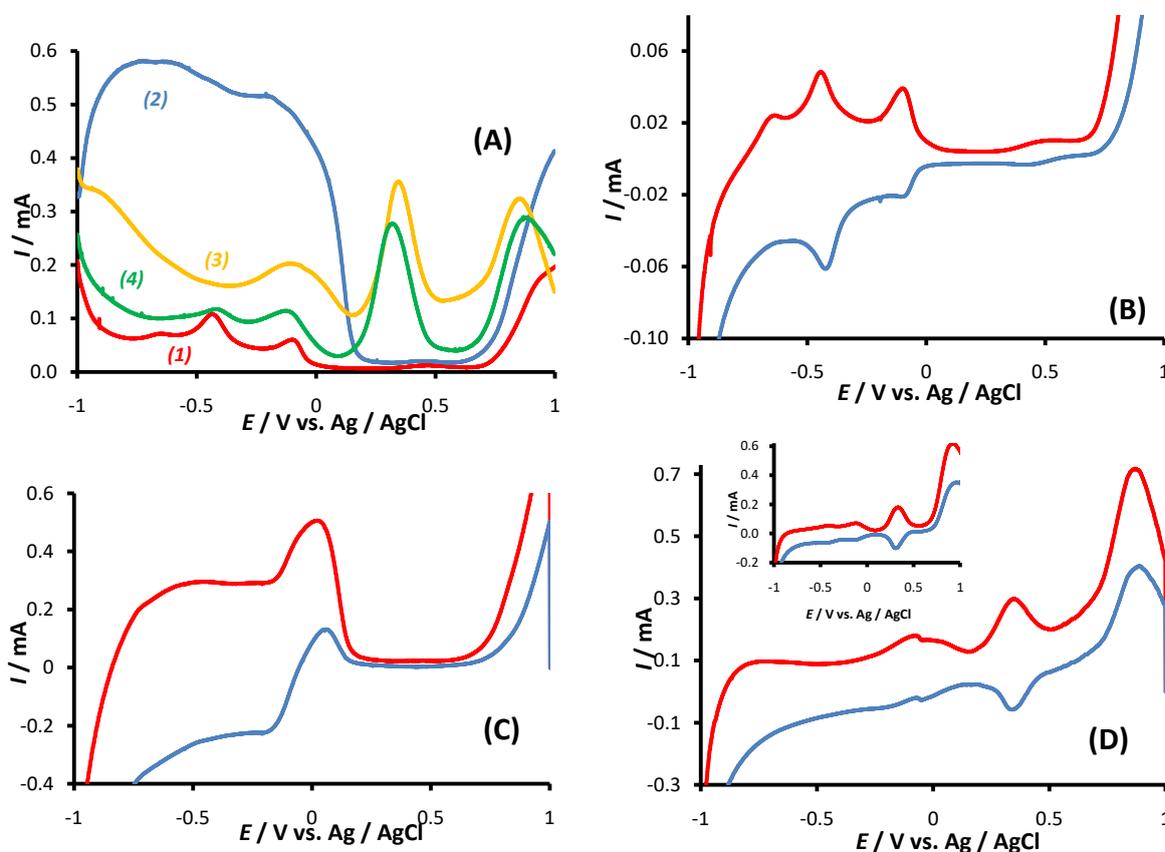


Figure 4. (A) Typical net SW voltammograms of (1) pyrite, (2) marcasite, (3) chalcopyrite_1 and (4) chalcopyrite_2. Corresponding forwards (red) and backwards (blue) components of (B) pyrite, (C) marcasite and (D) chalcopyrite_1. The inset of (D) refers to chalcopyrite_2. The parameters of the SW potential modulation are as follows: step potential $\Delta E = 1$ mV; SW amplitude $E_{sw} = 50$ mV; SW frequency $f = 10$ Hz, and starting potential $E_1 = -1.000$ V. Other conditions are same as in Fig. 1.

Apparently, although the elemental compositions of pyrite and marcasite are identical, their voltammetric profiles are markedly different and are correlated with the different crystal structures and chemical reactivities (curves **1** and **2** in Fig. 4A) [37]. Namely, let us recall that marcasite is the metastable, orthorhombic dimorph of FeS_2 in comparison to the more stable cubic form (pyrite) [39]. Thus, an important difference in stability between these minerals is expected in the region of the three-phase boundary line (i.e., electrode|mineral|electrolyte junction), hence assuming marcasite undergoes redox transformations at a rapid rate due to its higher reactivity [40].

In addition to the net SW component, a detailed inspection of the morphology of the forwards and backwards components of the SW voltammetric response enables further qualitative characterization and clear differentiation of the studied minerals, as shown in Fig. 4B-D. The forwards (oxidative) and backwards (reductive) components of the response reflect the nature of electrode processes (e.g., reversible and quasireversible chemical reactions, coupled electrode processes, etc.) [25]. The voltammetric features of pyrite evidently reveal a well-developed quasireversible character of the two electrode processes at formal potentials of approximately -0.450 and -0.050 V (Fig. 4B), related to the redox chemistry of iron species [26]. The marcasite voltammetric profile is markedly different from the voltammetric profile of pyrite (Fig. 4C), implying the catalytic character of the electrode reaction at approximately 0.000 V, which obviously might correlate with the higher chemical reactivity of marcasite compared to pyrite [41]. The voltammetric pattern of chalcopyrite (both samples 1 and 2, Fig. 4D) features a typical quasireversible electrode reaction at approximately 0.350 mV ascribed to the redox chemistry of the copper species, providing a clear means for qualitative voltammetric differentiation of the mineral.

The specific morphology of the voltammetric response of a mineral is related to a given set of parameters of the potential modulation (i.e., SW frequency, amplitude and step potential). Variation in the SW frequency, as the most critical time parameter in SWV, might significantly affect the voltammetric features. An example is given by the data in Fig. 5 for pyrite.

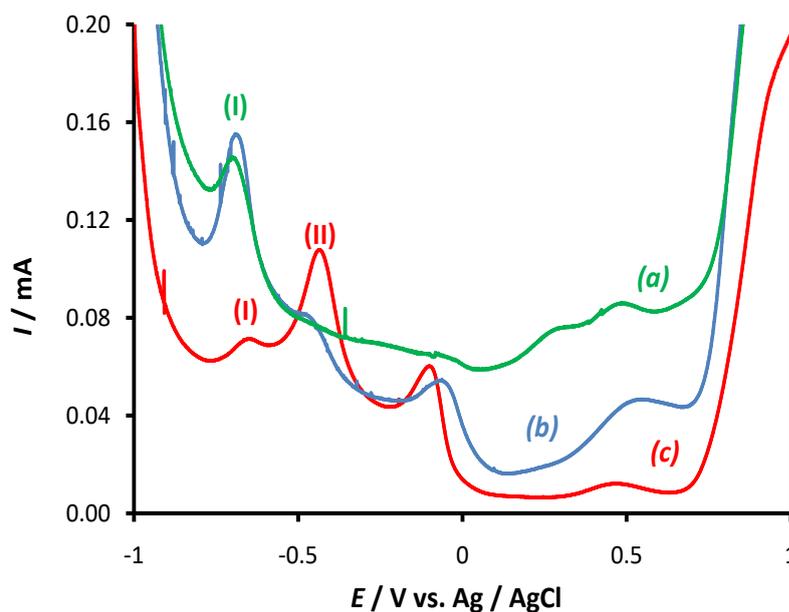


Figure 5. The effect of the SW frequency on the morphology of net SW voltammograms of pyrite. The SW frequency is: (a) $f = 100$ Hz; (b) $f = 50$ Hz, and (c) $f = 10$ Hz. Other conditions are same as in Fig. 4.

The net SW voltammograms are obviously different at frequencies of 100 Hz (fast experiment, curve (a) in Fig. 5) and at 10 Hz (slow experiment, curve (c)). For the fast experiment conducted at $f = 100$ Hz, the anodic stripping peak of elemental iron at approximately -0.600 V dominates (peak (I), electrode reaction (1)), while the extent of the follow-up chemical reaction (2) is insignificant. When the experiment is conducted at a slow rate ($f = 10$ Hz), the electrochemically formed $\text{Fe}^{2+}(\text{aq})$ by the stripping of elemental iron is transformed to $\text{FeS}(\text{s})$ (reaction 2), giving rise to electrode reaction (3), manifested as a well-developed net peak at -0.450 mV (peak (II), curve c, in Fig. 5), with a quasireversible electrochemical character (cf. Fig. 4B).

Overall, under defined experimental conditions, SWV provides a clear means for qualitative characterization of the studied minerals. Self-normalized net SW voltammograms are presented in Fig. 6 as final typical voltammetric profiles.

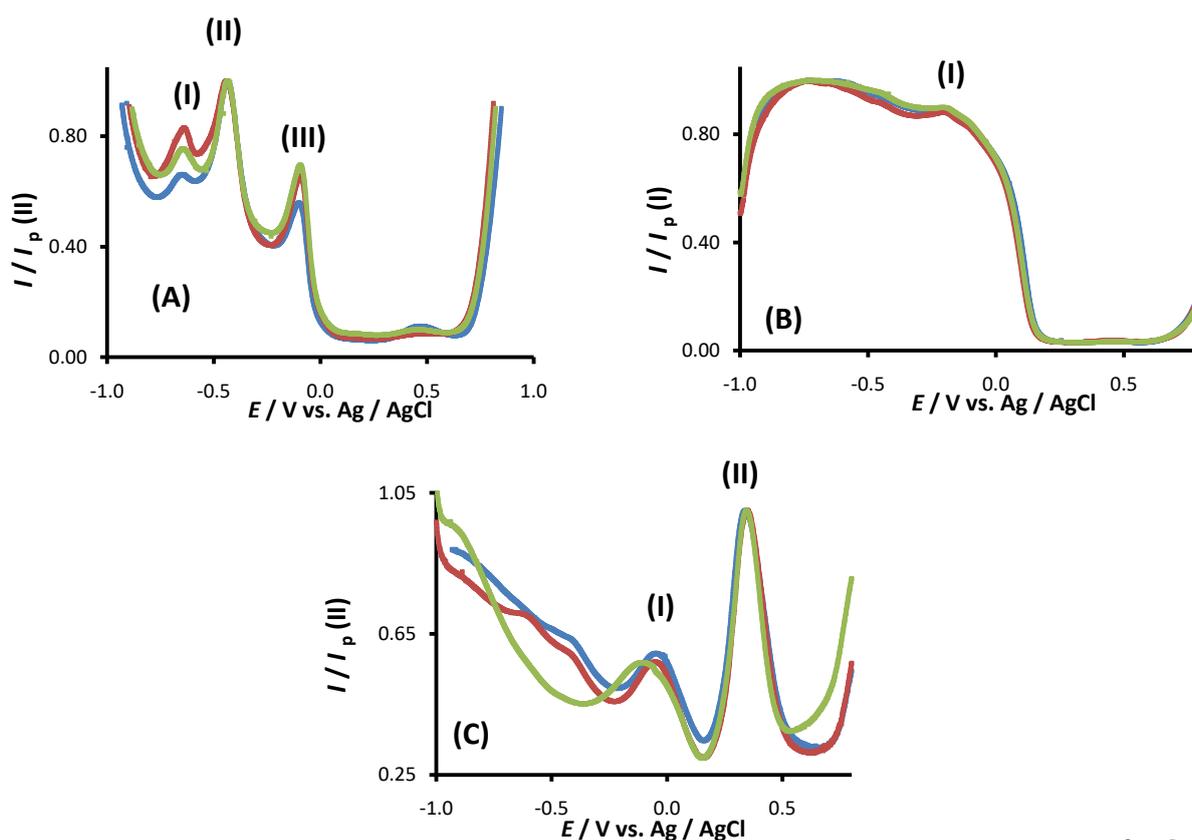


Figure 6. Typical self-normalized net SW voltammograms of (A) pyrite, (B) marcasite, and (C) chalcopyrite_1. Different colours represent different, repeating voltammograms recorded under identical conditions to demonstrate reproducibility of the SW voltammetric peaks. Self-normalization was performed by dividing all currents by the peak current of the most intense peak of each voltammogram, i.e., peak (II) for pyrite and chalcopyrite and peak (I) for marcasite. All other conditions are same as in Fig. 4.

Self-normalization is performed by dividing the net current values by the net peak current of the most intense peak in each voltammogram. In this way, the variation of the absolute peak current values in the voltammetry of solid microparticles due to varying amounts of immobilized particles [16]

can be circumvented. Thus, the position of the voltammetric peaks and the relative ratio of the peak intensity can be reliably compared and used for qualitative characterization. Table 2 lists the typical parameters of each normalized voltammogram, calculated as averaged values of five measurements, presenting the peak potential values and the relative peak intensity.

Table 2. Typical parameters of the self-normalized net SW voltammograms presented in Figure 6. The average values and the relative standard deviation of each peak were calculated by repeating the experiment five times.

Mineral	Peak I		Peak II		Peak III	
	Peak potential E	Relative Intensity	Peak potential E	Relative Intensity	Peak potential E	Relative Intensity
Pyrite	-645.0 mV \pm 4.5 mV	0.084 \pm 0.035	-438.5 mV \pm 3.8 mV	0.4273 \pm 0.0322	-97.0 mV \pm 2.6 mV	0.389 \pm 0.062
Marcasite	-217.6 mV \pm 9.1 mV	0.859 \pm 0.008	/	/	/	/
Chalcopyrite_1	-66.9 mV \pm 28.7 mV	0.189 \pm 0.015	342.6 mV \pm 5.0 mV	0.6736 \pm 0.0185	/	/

4. CONCLUSIONS

Square-wave voltammetry of solid microparticles is a simple and powerful experimental methodology for fast, in situ, qualitative characterization of mineral particles by means of cheap electrochemical instrumentation, complementing conventional techniques for mineral characterization, such as FTIR spectroscopy and X-ray diffraction. While the latter two techniques depend straightforwardly on the structure of the solid sample, voltammetry depends on the redox and chemical reactivity of the solid sample driven by a flux of electrons supported by the working electrode. Accordingly, despite experimental simplicity, the outcome of electrochemical experiments is a result of highly complex physicochemical phenomena.

The experimental data presented additionally support the known fact that cyclic voltammetry is highly suited for mechanistic analysis of electrode reactions of studied minerals; however, the voltammetric outcome strongly depends on the methodology of the experiment, while the complexity of voltammetric profiles is hardly suited for qualitative differentiation. However, square-wave voltammetry, which has a high speed, sensitivity and superior resolution, enables obtaining specific voltammetric profiles, which can be used as voltammetric fingerprints for qualitative characterization of the studied minerals. The intrinsic nature of the SW voltammetric experiment, consisting of repetitive, reductive and oxidative potential pulses applied during a single voltammetric scan, results in specific, well-defined and reproducible voltammetric profiles. At the beginning of the SW voltammetric experiment starting from -1.000 V (vs. Ag/AgCl), a specific reaction mixture is formed in the vicinity of the three-phase boundary region (mineral|electrode|electrolyte), consisting of reduced

products of the mineral and the native yet unconsumed mineral microparticles, resulting in voltammetric profiles that are specific for structurally different pyrite and marcasite, despite their identical chemical composition. The difference with chalcopyrite is even more obvious due to the additional redox chemistry of copper species. Finally, the simple self-normalization of net SW voltammograms results in even more specific voltammetric profiles, in which a sole relative intensity of voltammetric peaks can be defined, independent of the number of solid particles immobilized on the electrode surface.

ACKNOWLEDGEMENTS

Financial support through NATO Grant No. SPS G5550 is acknowledged with gratitude.

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