

Electrochemical Characteristics of Natural Mineral Covellite

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ABSTRACT

Electrochemical characteristics of covellite (CuS) are of importance from flotation and metallurgical point of view, as well as due to its potential application in solid state solar cells and in photocatalytic reactions. Also, the compound CuS appears as an intermediary product or a final product in electrochemical oxidation reactions of chalcocite (Cu₂S) which exhibits supercapacitor characteristics. Natural copper mineral covellite has been investigated in inorganic sulfate acid electrolytes, as well as in strong alkaline electrolyte. Physical properties of covellite were characterized by X-ray diffraction (XRD) and the active surface was examined by optical and electron microscopy (EM) before and after oxidation in galvanostatic regime. Different electrochemical methods (galvanostatic, potentiostatic, cyclic voltammetry and electrochemical impedance spectroscopy—EIS) have been used. The capacitance of around 21 Fcm⁻² (geometric area), serial resistance of about 90 Ωcm² and leakage resistance of about 1200 Ωcm² have been measured in 1 M H₂SO₄. The addition of cupric ions in sulfate electrolyte leads to the significant increasing of the capacitance, but having the increase of self-discharge as a negative side phenomenon. The capacitance of around 6.7 Fcm⁻² (geometric area), serial resistance of about 80 Ωcm² and leakage resistance of about 380 Ωcm² have been measured in 6 M KOH.

Keywords: Covellite; Capacitance; Copper Sulfides; Electrochemical Characterization; Solar Cells

1. Introduction

Copper sulphides were largely investigated in the recent years due to the interesting optical and electrical properties, resulted from the variations in stoichiometry, composition, morphology, and due to their potential applications in various fields such as absorbers for solid state solar cells or in photocatalytic reactions [1]. Solid-state solar cells are considered attractive devices for the next generation of photovoltaic cells. Copper sulfides can be considered in some ways ideal absorber materials—being non-toxic, cheap and, importantly, abundant, and with good absorption characteristics. An ETA (Extremely Thin Absorber) cell is one of the few configurations with potential to exploit the favourable qualities of CuS in a low-cost solar cell. Additionally, CuS can be considered a model electronically “poor” semiconductor, and construction of a good solar cell with it would be clear proof of the ETA principle [2].

It was found that different natural sulfide minerals such as pyrite (FeS₂) [3] and chalcocite (Cu₂S) [4], as well as metal sulfides obtained by chemical precipitation, like cobalt sulfide [5] or nano SnS [6] and ZnS [7], exhibit capacitance characteristics in aqueous solutions of

some acids and alkaline. Compound CuS appears as an intermediary product or a final product in electrochemical oxidation reactions of chalcocite which exhibits supercapacitor characteristics. The common characteristic of sulfides exhibiting high capacitances is that their metal constituent can appear in two or more valence states. Also, while modeling anodic oxidation reaction of covellite, it was established that the equivalent electrical circuit has to contain one relatively high capacitor [8]. Those facts were the reason for examination of the mineral covellite capacitive characteristics.

Covellite is a copper mineral that can be found in some copper mines as the relatively pure massive samples. Its chemical composition is between CuS and Cu_{1.1}S. Natural covellite has a hexagonal crystal lattice with the parameters $a_0 = 0.3972 \pm 0.0001$ nm and $c_0 = 1.6344 \pm 0.01$ nm, but sometimes it can appear as monoclinic [9]. Natural covellite is a semiconductor, but its electrical resistivity is in order of magnitude 10⁻⁶ Ωm, that is near to metals [10,11]. It was proved by thermoelectric probe that covellite is a p-type semiconductor [12] and confirmed by photoelectrical testing of the samples from Bor copper mine [13]. Most results of electrochemical investigations of copper minerals can be found

in older literature, but mainly from the metallurgical point of view [14-26]. Yin *et al.* [27,28] investigated behavior of covellite and other copper sulfides with emphasize on their oxidation in alkaline solutions.

2. Experimental

The applied standard electrochemical methods such as galvanostatic, cyclic voltammetry, potentiostatic method and impedance spectroscopy (EIS), and other methods of material characterization (optical and scanning electron microscopy) were described elsewhere [3,8,13,25,29-33].

2.1. Equipment

The electrochemical characterization was carried out by a standard three-electrode system consisting of saturated calomel electrode (SCE) as a reference electrode, platinum as a counter electrode and a number of working electrodes the active part of which is the tested material. The contact between the copper wire and the electrode material was achieved by using conducting silver glue, and then mounted in acrylic mass for cold mounting. The working electrodes (five of them) were of 18 - 49 mm² and counter electrode of 200 mm² of active surface area.

The system for electrochemical measurements consisted of hardware (PC, AD-DA converter NI 6251 from National Instruments and analog interface developed on Technical faculty in Bor) and software for excitation and measurement (LabVIEW platform and application software) [33].

The optic microscopy of electrode material was carried out by using LOMO MIN9 microscope with digital camera JENOPTIK ProgRes C10+ for the immediate records transfer into the computer. The electronic microscopy was performed by using JSM 35 microscope. The X-ray analysis was done by Siemens diffractometer Kristalloflex 810.

2.2. Materials

The starting material was samples of natural copper mineral covellite from Bor copper mine. The first series of experiments was done in unimolar aqueous solutions of sulfuric acid with or without the addition of copper sulfate. The experiments in the second series were performed in strong alkaline solution (6 M KOH). Analytical grade reagents (sulfuric acid, copper sulfate and potassium hydroxide made by "Zorka" Šabac, Serbia) were used without further purification. Solutions were prepared with distilled water and were not de-aerated.

The polished surface of the material was analyzed by optic and electronic microscopy, before and after the application of galvanostatic impulse of 0.5 mA for the duration of 40 s in 1 M H₂SO₄ electrolyte. **Figures 1(a)** and **1(b)** show optic microscopy pictures of non-treated (a) and treated (b) covellite. Uniform surface of the

non-treated sample confirms its high purity concerning natural mineral; natural minerals usually contain some impurities like quartz or pyrite. It is obvious from **Figure 1(b)** that some product appeared on the treated electrode surface during the anodic process. The structure of this product may be considered as the main reason of relatively high capacitance found out at covellite and other copper minerals, especially chalcocite.

The chemical composition of the material was determined by X-ray diffraction analysis of numerous samples, one of which is presented by the diagram in **Figure 2**. The pattern shows that the main constituent of the sample is compound CuS.

2.3. Procedures

For each set of experiments working electrodes were ground, polished, washed out, dried and, finally, submerged into electrolyte fresh made for each series of experiments. Polishing and washing out (without grinding) was done between two experiments. Grinding was performed by the finest grinding paper, polishing by alumina (0.05 μm) and washing out by distilled water and alcohol.

All the experiments were performed at room temperature. Having submerged the working electrode, its potential versus the reference electrode was observed, and, after stabilization, the value of the rest potential was

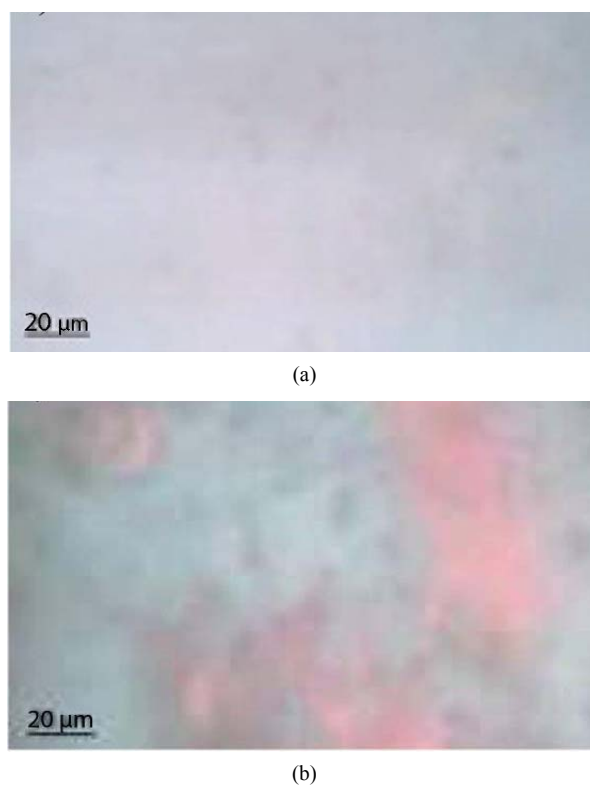


Figure 1. Microscopic picture of non-treated (a) and treated (b) covellite.

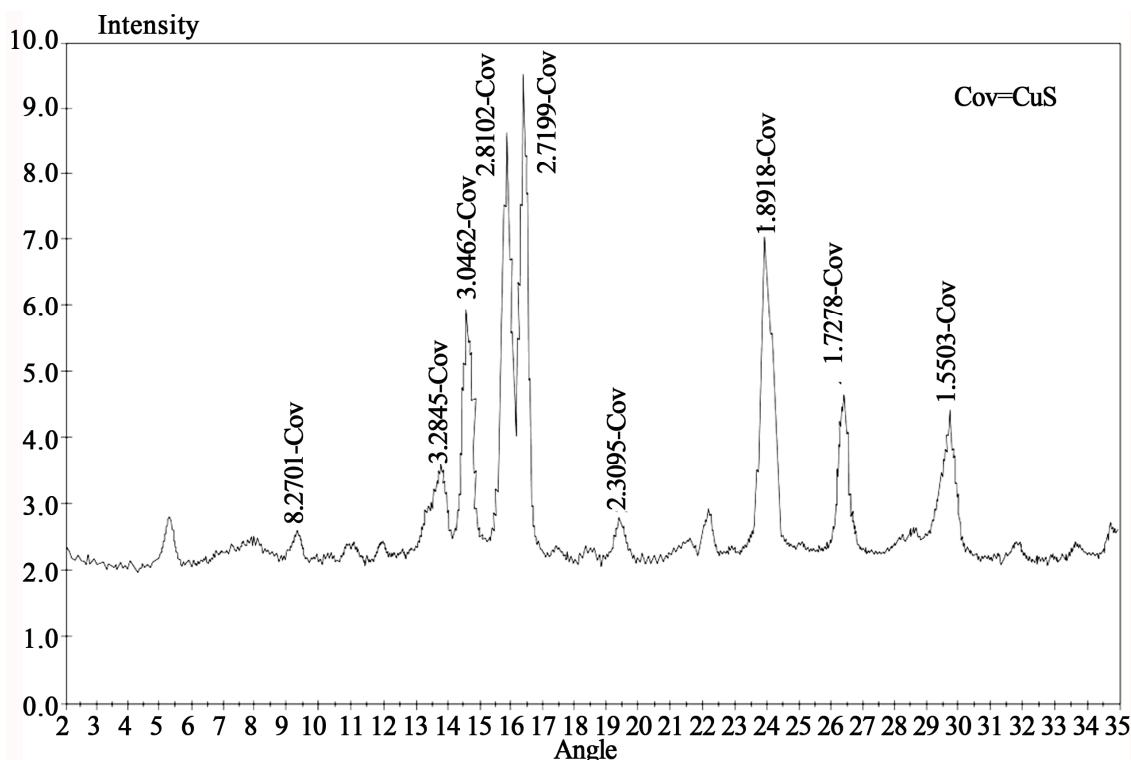


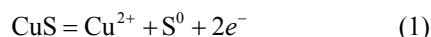
Figure 2. X-ray diffraction pattern of natural mineral covellite.

noted down. The value was used to determine parameters of subsequent experiments depending on the method of examination.

3. Theoretical Part

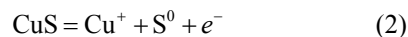
3.1. Possible Reaction Mechanisms

Oxidation of a sulfide mineral is a multi step process made up of a series of consecutive reactions. In literature [12-25] it can be found a series of assumptions about the mechanism of electrochemical oxidation of copper sulfides chalcocite and covellite. Most authors confirm that the overall reaction of anodic dissolution of covellite in acid solutions is:

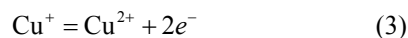


Electronic microscopy confirms the presence of elemental sulfur on the surface of anodically treated covellite, but there is very low probability of the two electron transfer in one step because the activation energy of such reactions is very high in compare to one electron transfers. Also, that reaction is almost completely irreversible.

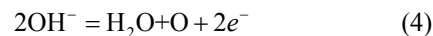
More probable mechanism consisting of two one-electron steps is:



followed by:



Some authors [14] presume that the first step is the discharge of hydroxide ions and oxygen evolution at CuS:



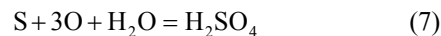
Further dissolution in acid and weak alkaline solutions proceeds by chemical oxidation of CuS with atomic oxygen produced in previous step:



Elemental sulfur also can be oxidized with atomic oxygen, which is very reactive:

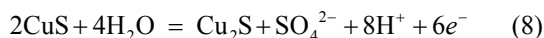


or



Previous investigations performed mainly in acid solutions [8,13,23,25] lead to the assumption that the metal ions from the mineral crystal lattice are transferred into the solution leaving a surface region with the higher content of sulfur. That sulfur can be treated as adsorbed species giving rise to the pseudocapacitance exhibited by CuS and Cu₂S.

In strong alkaline solutions covellite is thermodynamically instable compound, as well as elementary sulfur. Because of that, in a medium of this kind, the reaction (4) may be followed by:



All product species in the reaction (8) are thermodynamically stable in strong alkaline solutions [10].

3.2. Equivalent Electrical Circuit

In a goal to achieve mathematical analysis of the measured data, it was necessary to develop mathematical model adapted to the investigated class of electrochemical system and it is strongly connected with the physical parameters of the system. Adopted equivalent circuit in a general case is given in **Figure 3(a)**. R_0 corresponds to the resistance of electrolyte and electrode material, and its value is in order of magnitude milliohm ($\text{m}\Omega$) or ohm (Ω). Capacity C_0 corresponds to double layer formed on the electrolyte side. Resistances R_1 and R_2 (order of magnitude ohm to dozen ohms) are related to slow processes of adsorption and diffusion, as well as the capacitances C_1 and C_2 . As a matter of fact, the branch R_1C_1 exhibits and describes the inconstancy of parameters in R_2C_2 branch. R_3 is resistance of self-discharging, meaning that it is reciprocal to leakage current. Its value is in order of hundred ohms till the dozens of kilo ohms.

The equation for impedance for equivalent circuit given in **Figure 3(a)** is complex and not enough clear. So, knowing the nature of the process, *i.e.* orders of magnitude of the circuit parameters, much simpler circuit is applied for analysis and characterization of systems like investigated here. The scheme of that system is presented in **Figure 3(b)**, R_s being total serial resistance of the system, C —integral capacitance, R_L —parallel resistance of self discharge (leakage).

4. Results and Discussion

The next electrochemical methods have been used: galvanostatic, cyclic voltammetry, potentiostatic method and impedance spectroscopy (EIS). In a goal to determine the main parameters, investigated electrochemical system was modeled by a simplified equivalent circuit which consisted of a main capacitance, a serial resistance and leakage resistance [25,34].

4.1. Galvanostatic Examination

Classic galvanostatic method assumes that the system is excited by the constant current between working and as the system response. Besides the classical, the modified method [32,34] with prolonged duration of current impulse is applied in order to allow the overwhelming system analysis. The surface of the electrode is also analyzed before and after the use of galvanostatic impulse.

Figure 4 shows an electronic microscopy picture of the covellite sample before and after the application of

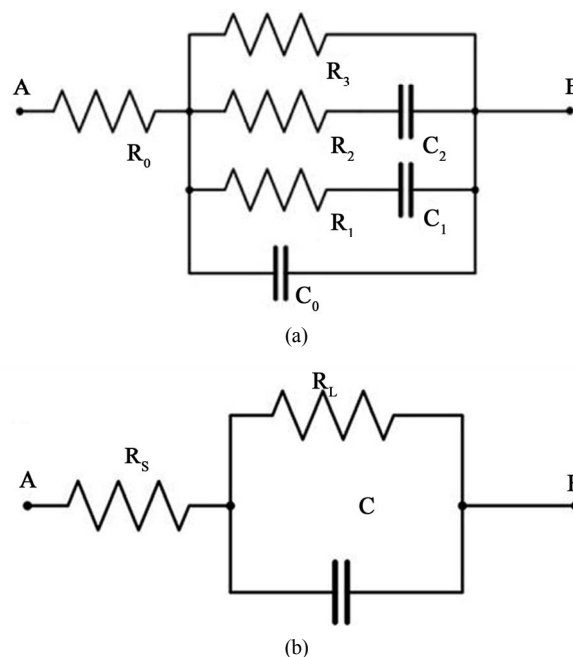


Figure 3. Equivalent electrical circuit; (a) complete, (b) simplified.

galvanostatic impulse of 0.5 mA for the duration of 40 s in 1 M H_2SO_4 electrolyte. The consequences of the reaction on the treated samples are obvious so as their non-homogeneous surface layer, noticeably porous, hence the increase of the electrode interface.

A series of experiments in the 0.5 M H_2SO_4 + 1 M NaCl electrolyte showed the intense self-discharge effect (electrodes tend to relax quickly), so the project was abandoned.

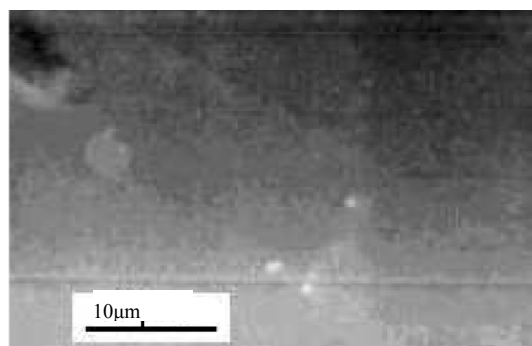
All the prepared electrodes were first examined in the unimolar solution of pure sulfuric acid (1 M H_2SO_4). Galvanostatic curve for the covellite electrode (surface area 0.38 cm^2) subjected to excitation of 0.1 mA for the duration of 80 s in the solution of unimolar sulfuric acid is given in **Figure 5**. Serial resistance of about $90 \Omega\text{cm}^2$ has been determined from the diagram.

Galvanostatic investigations with the same electrodes have been performed in a strong alkaline solution, as well. Galvanostatic curve for the covellite electrode (surface area 0.42 cm^2) subjected to excitation of 1 mA for the duration of 80 s in the solution of 6 M KOH is given in **Figure 6**. Serial resistance of about $80 \Omega\text{cm}^2$ has been determined from the diagram.

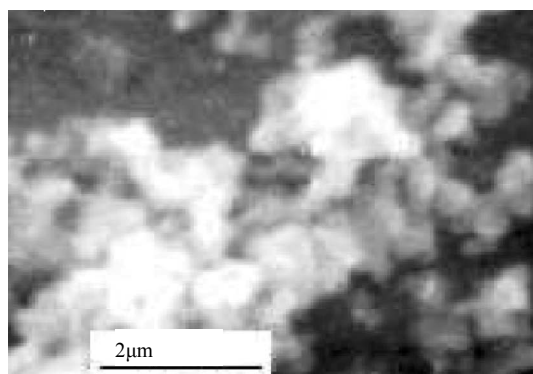
4.2. Cyclic Voltammetry

Since the standard cyclic voltammetry method is very convenient for capacitance measurements, a series of experiments was carried out in various electrolytes.

Figure 7 presents a series of voltammograms obtained in 1 M H_2SO_4 by cycling with the sweep rate of 5 mVs^{-1} .



(a)



(b)

Figure 4. Electronic microscopy picture of non-treated (a) and treated (b) covellite.

It can be seen that the voltammetric current shows a steady decrease with the increasing of cycle numbers. The existence of a compact solid reaction product remaining on the electrode surface may be considered as the main reason of that decrease. That product causes a slow diffusion in solid state, which leads to the increase of serial resistance and controls further reaction. Capacitance calculated from the first loop surface area is around 20.6 Fcm^{-2} (electrode active surface area 0.42 cm^2).

Figure 8 shows voltammetric curves of covellite electrode in 6 M KOH solution obtained using a sweep rate of 5 mVs^{-1} . Capacitance calculated from the third loop is around 6.7 Fcm^{-2} (electrode active surface area 0.42 cm^2).

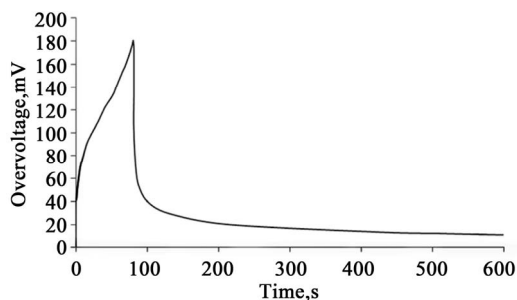


Figure 5. Galvanostatic curve of covellite in 1 M H_2SO_4 aqueous solution; excitation 0.1 mA, 80 s; active surface area 0.38 cm^2 .

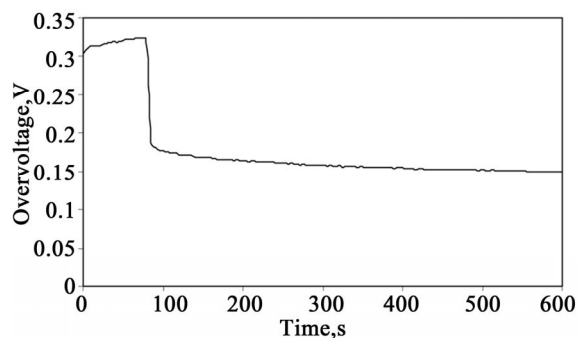


Figure 6. Galvanostatic curve of covellite in 6 M KOH aqueous solution; excitation 1 mA, 80 s; active surface area 0.42 cm^2 .

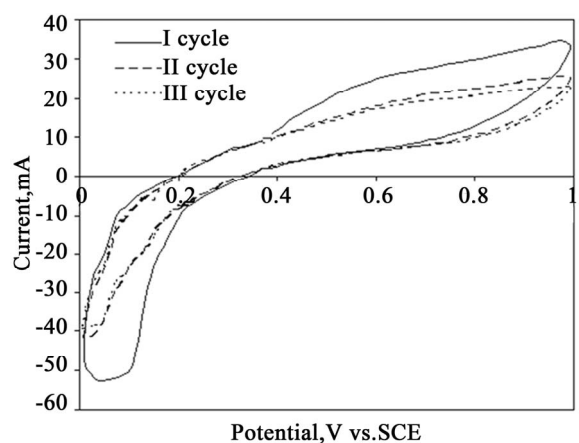


Figure 7. Cyclic voltammograms of covellite in 1 M H_2SO_4 at $v = 5 \text{ mVs}^{-1}$.

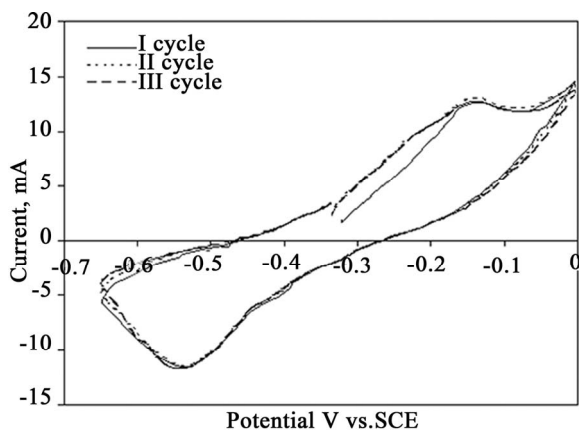


Figure 8. Consecutive cyclic voltammograms of covellite in 6 M KOH at $v = 5 \text{ mVs}^{-1}$.

4.3. Potentiostatic Research

The advantage of potentiostatic method—relatively short duration of the experiment—was made use of for the detailed investigation of the electrode material behavior in various electrolytes for the purpose of optimum electrolyte distinction concerning the obtention of maximum capaci-

tance and minimum leakage current.

Potentiostatic curves of covellite electrode in the solution of 1 M H_2SO_4 for excitation period of 100 s by the voltage of 20 and 100 mV are presented in **Figure 9**. It was proved that the self-discharge resistance practically does not depend on overvoltage (5000Ω at $\eta = 100$ mV and 5400Ω at $\eta = 20$ mV), while leakage current is $4 \mu\text{A}$ at 20 mV and $18.5 \mu\text{A}$ at 100 mV.

Potentiostatic curves obtained in electrolyte containing 1 M $\text{H}_2\text{SO}_4 + 0.1$ M CuSO_4 at the electrodes made of the same covellite sample, but with different surface area are presented in **Figure 10**. The curves confirm the supposition that the serial resistances are inversely dependent to the electrode surface area.

4.4. Electrochemical Impedance Spectroscopy (EIS)

Since EIS, if applied on the systems containing high capacitances, demands long duration of experiments [33] just few characteristic electrochemical systems were examined by this method.

Figure 11 shows the impedance diagram of covellite electrode in the solution of 1 M H_2SO_4 . The excitation voltages were $V_{\text{DC}} = 20$ mV, $V_{\text{ACmax}} = 5$ mV. From the diagram it was obtained a capacitance of 22 Fcm^{-2} , serial resistance of $93 \Omega\text{cm}^2$ and leakage resistance of $1160 \Omega\text{cm}^2$.

Figure 12 shows the impedance diagram of covellite electrode in the solution of 6 M KOH. The alternate excitation voltage was $V_{\text{ACmax}} = 7$ mV, without the DC offset ($V_{\text{DC}} = 0$ mV). From the EIS diagram it was obtained a capacitance of 9.3 Fcm^{-2} , which is in agreement with the value obtained from the cyclic voltammetry measurement. Also, from the same diagram it was obtained a serial resistance of $82 \Omega\text{cm}^2$ and leakage resistance of $380 \Omega\text{cm}^2$.

The addition of copper ions in the electrolyte results in the significant increasing of capacitance of investigated mineral. The same effect was noticed at the natural

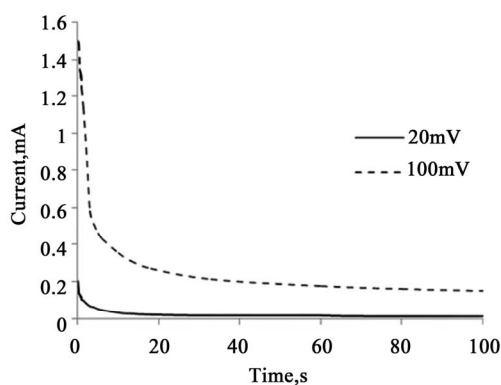


Figure 9 . Potentiostatic curves of covellite electrode in the solution of 1 M H_2SO_4 .

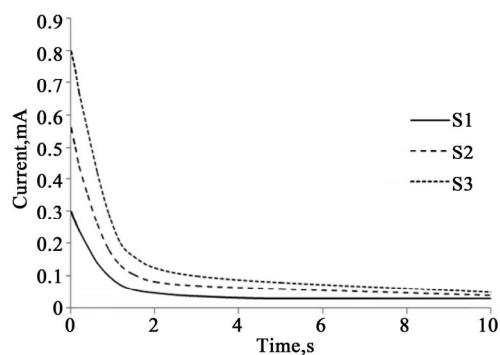


Figure 10. Family of potentiostatic curves for various electrode surface area (S1 = 33 mm^2 ; S2 = 43 mm^2 ; S3 = 49 mm^2).

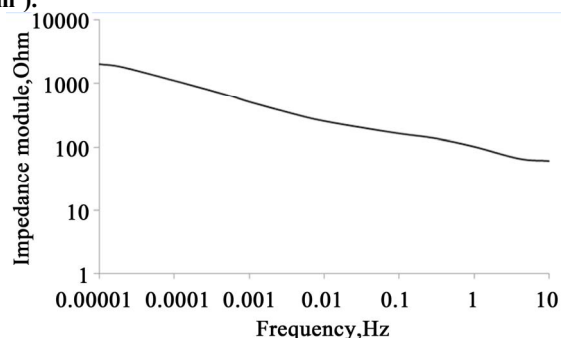


Figure 11. Impedance diagram for covellite electrode in 1 M H_2SO_4 .

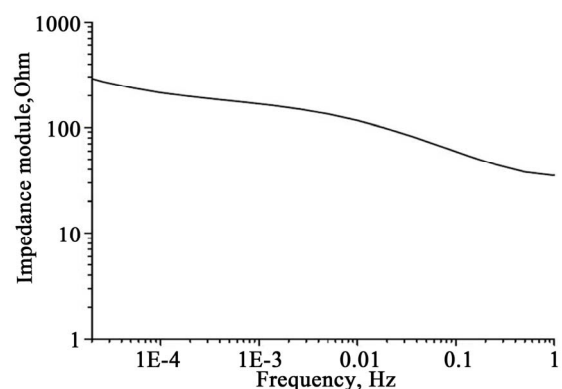


Figure 12. Impedance diagram for covellite electrode in 6 M KOH.

copper sulfide mineral chalcocite—it was determined that its capacitance increases with the concentration of CuSO_4 , but having the increase of self-discharge as a side phenomenon, so the optimum concentration was estimated to be 0.1 M CuSO_4 [4].

5. Conclusions

The investigations using different electrochemical methods showed that natural copper mineral covellite exhibits relatively high capacitivity in order of magnitude of 20 Fcm^{-2} during the first anodic polarisation in acidic so-

lutions. In the next polarisation phases, the product formed at the electrode surface causes a slow diffusion in solid state that leads to the increase of serial resistance and controls further reaction. The existence of a compact solid reaction product remaining on the electrode surface was proved by electron microscopy.

In alkaline solution covellite exhibits a capacitance of the same order of magnitude, although for about three times lower; at the same time leakage, *i.e.* self-discharge is bigger. The investigations on covellite in acidic and alkaline solutions had a goal to enable optimization of the electrochemical systems in the sense to obtain performances as high as possible (usually the lowest serial and biggest parallel resistance at the same time).

6. Acknowledgment

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