

Paweł NOWAK\*, Barbara KOZIOL\*\*

## ON THE REST POTENTIAL OF PYRITE ELECTRODE IN OXYGEN-FREE SOLUTIONS OF IRON (II) SULFATE<sup>1</sup>

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The exchange current density (ECD) for the reaction:  $Fe_{1+y}S_2 = Fe_{1+y-x}S_2 + xFe^{2+} + 2xe^-$  was estimated measuring the impedance of pyrite electrodes in the solutions of iron (II) sulfate. For five different pyrite electrodes,  $0.5 \text{ mol dm}^{-3}$   $FeSO_4$  solution and potentials close to the potential of the reaction  $FeS_2 = Fe^{2+} + 2S^0 + 2e^-$  the ECD was found to be between 8 and  $15 \mu\text{A cm}^2$ . Low value of the ECD causes that the potential of pyrite electrode in solutions of iron (II) sulfate does not attain the equilibrium value (i.e. the value within the range of pyrite thermodynamic stability) except the most concentrated and very well deoxidized solutions. For the concentrations of  $FeSO_4$  solution lower than  $0.5 \text{ mol dm}^{-3}$  pyrite electrode shows the rest potential outside the limits of thermodynamic stability, which means that the measured potential is a mixed (corrosion), not equilibrium potential.

*Key words: pyrite, pyrite electrochemistry, impedance spectroscopy*

### INTRODUCTION

Pyrite is undoubtedly the most abundant sulfide mineral in the earth crust. Pyrite accompanies almost all other sulfides and many non-sulfide minerals (including coal) and the separation of pyrite from other minerals (especially from coal) by flotation is a process of extreme importance (Tao et al., 1993). In hydrometallurgy the presence of pyrite in the raw material being processed influences strongly the process because the oxidation of pyrite generates sulfuric acid and iron (III) ion, the later being a strong oxidant (Dutrizac and MacDonald, 1974). In oxidizing environment pyrite exhibits

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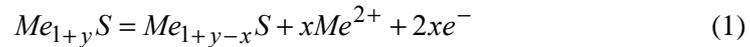
\*Polish Academy of Sciences, Institute of Catalysis and Surface Chemistry, ul. Niezapominajek 8, 30239, Kraków, Poland

\*\*Undergraduate student, Jagiellonian University, Faculty of Chemistry

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high rest potential, usually higher than other sulfide minerals, inducing galvanic effects both in flotation as well as in hydrometallurgy (Nowak et al., 1984).

A lot of pyrite may be found in the environment either as natural constituent of the rocks or as a waste product, left at the disposal places. The oxidation of those pyrite liberates sulfuric acid and toxic metal ions, creating problems in the environment protection (Jambor et al., 2000). So, it is not surprising that the literature on the pyrite oxidation is very rich (Peters, 1977, Hiskey and Schlitt, 1982, Lowson, 1982, Williamson and Rimstidt, 1994). Despite the vast body of literature on the subject there are many problems, connected with pyrite oxidation which require further elucidation. One of such problems is the path of the sulfide sulfur oxidation. Some authors (see Wei, 1997, and references cited therein) think that the formation of sulfates and elemental sulfur are two independent processes, proceeding through intermediate lower-valence sulfur species. The other authors (Hamilton and Woods, 1981) proposed that elemental sulfur is the primary product of pyrite oxidation. According to Buckley and Woods (1987) and Buckley and Walker (1988) the oxidation of pyrite (and other sulfides) begins with the creation of metal-depleted sulfide which eventually rearranges further to elemental sulfur and stable sulfide phase. Such mechanism of sulfur formation during oxidation of copper sulfides was proposed by Filmer et al. (1979). Therefore, the initial stage of a metal sulfide anodic dissolution may be described by the equation:



Most of sulfide minerals are pure electronic or mixed ionic-electronic conductors and show the tendency to non-stoichiometry (Shuey, 1975). Binary compounds of pure ionic conductivity (silver halides, for example) together with the parent metal of the binary compound form the second type electrodes of electrode potentials quite stable in the solutions containing the ions of either metal or nonmetal constituting the binary compound. Contrary, the potential of a metal sulfide electrode in the solution of either metal or sulfide ions shows usually variability. Sato (1966) discussed the problem long time ago. For the binary sulfide of the composition  $Me_{1+y}S$  the potential of a sulfide electrode in the solution of either metal or sulfide ions may be described, according to Sato, by the equation:

$$E_{MS} = E_{MS}^0 + \frac{RT}{4F} \ln \frac{a_{M_{aq}^{2+}} a_{S_{MS}}}{a_{S_{aq}^{2-}} a_{MS}} \quad (2)$$

where  $a_{M_{aq}^{2+}} (a_{S_{aq}^{2-}})$  is the activity of a metal (sulfide) ion in the solution and  $a_{M_{MS}} (a_{S_{MS}})$  is the activity metal (sulfur) in the sulfide phase, and

$$E_{MS}^0 = \frac{E_{M,M^{2+}}^0 + E_{S^{2-},S}^0}{2}, \text{ where } E_{M,M^{2+}}^0 \text{ is the standard potential of the metal in}$$

the solution of metal ions and  $E_{S^{2-},S}^0$  is the standard potential of sulfur in the solution of sulfide ions. So, the potential of a metal sulfide electrode in the solution containing either metal or sulfide ions of fixed concentration (note that if one of the concentrations is given, the activity of the other ion is fixed by the solubility product relation) may attain the value within two limits. The lower limit is determined by the condition:  $a_{M_{MS}} = 1$  (metal-rich sulfide or sulfide in equilibrium with the other sulfide phase of higher metal content). The higher limit is determined by the relation:  $a_{S_{MS}} = 1$  (sulfur-rich sulfide or sulfide in equilibrium with the other sulfide phase of higher sulfur content).

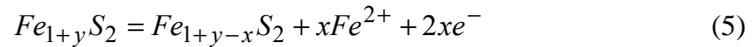
Pyrite is a special case because it is a disulfide and the equilibrium is established with  $S_2^{2-}$  ions, not with  $S^{2-}$  ions, but the situation should be similar. Considering the possible reactions, the potential of a pyrite electrode in the solution of  $Fe^{2+}$  ions should attain the value between the potential of the reaction:



and the potential of the reaction:



depending on the exact composition of the mineral surface. Between those two limits the only electrochemical reaction which can carry the electrical charge through the interface (unless other redox couples are present either in the solution or at the surface) is the reaction:



The exchange current density for the reaction (5) might be measured which would allow the estimation of the rate of this reaction. An ideal method for this purpose seems to be electrochemical impedance spectroscopy (EIS) since this method allows one to measure the rate of an electrochemical reaction at the equilibrium potential without extensive polarization of the interface. Note that when reaction (5) proceeds the composition of the surface changes continuously and, hence, the rate constant of the reaction may also change gradually. Therefore, the methods in which rather high charge is flowing through the surface, like linear polarization method, cannot be applied in that case.

## EXPERIMENTAL

The impedance spectra and the voltammograms have been measured using 1250 Frequency Response Analyzer and 1286 Electrochemical Interface (Schlumberger-Solartron). The impedance data were subsequently processed by fitting the parameters of a proper electrical equivalent circuit (EEC) to experimental data using the MINUIT program (James and Roos, 1975). Five pyrite samples, all museum grade manocrystals, were used in the experiments. One of the pyrite samples was from the ore deposits in Huanzala, Peru, supplied by Wards Sci. Establishment, the other samples were also mineral pyrites from ore deposits in Ural mountains, from ore deposits in Elba (Italy) and in Rio Tinto (Spain). One sample was a coal-pyrite sample from the coal deposits in Poland (Halemba coal mine). The crystals were cut with a diamond saw to dimensions approximately  $0.5 \times 0.5 \times 0.5 \text{ cm}^3$  and cubic shape and embedded at the end of a glass tube with an epoxy resin. Before the measurements the exposed surface of the crystal was polished on SiC emery papers ending with the 4000 grade. Because the extensive polishing may significantly influence the surface properties of the mineral (Libowitzky, 1994, Mendiratta et al., 1996) the polishing was performed very gently. Water purified by catalytic pyrodistillation (Conway et al., 1973) was used for preparation of the solutions. Solutions were bubbled with argon before the measurements to remove oxygen. All reagents used were of analytical reagent purity grade.

Typical electrochemical cell in three electrode configuration with saturated calomel electrode as a reference electrode and platinum wire as a counter electrode was used. Some pyrite samples exhibited high resistance and rectifying properties. In that case the potentiostat was operated in a four-electrode mode with the "Reference 2" electrode connected to a potentiometric contact on the side surface of the pyrite sample (Peters, 1977).

The iron (II) sulfate, used in the experiments was recrystallized just before the start of experiments and kept tightly covered. The salts of divalent iron contain always traces of trivalent iron, which may oxidize the surface of pyrite electrode. So, the experiments were performed in the following manner. Iron (II) sulfate was dissolved in the  $0.5 \text{ mol dm}^{-3}$  solution of sodium sulfate of the pH of 1.85. The  $\text{Na}_2\text{SO}_4$  solution was deoxidized previously by bubbling with argon. pH was chosen not too low to prevent the spontaneous dissolution of pyrite and not too high to prevent the formation of oxides at the surface (Sato, 1992).

In a separate beaker a portion of metallic iron powder (about 0.5 g) was washed with deoxidized  $0.5 \text{ mol dm}^{-3}$  sulfuric acid solution to remove oxides from the surface. Iron powder was finally washed with a portion of methanol (to remove water), dried and introduced to the cell with the solution of iron (II) sulfate. The powder in the cell was agitated with the magnetic stirrer and the value of the redox potential (measured with the Pt electrode) was continuously registered. The pyrite electrode was not introduced to the solution before the attainment of the redox potential lower than the

potential of the redox couple  $H^+/H_2$ . The lowest registered potentials were about  $-0.15$  V. Note that the standard potential of the  $Fe^{2+}/Fe^{3+}$  redox couple is very high ( $+0.771$  V, according to Heusler, 1985), so at the registered potential the concentration of trivalent iron would be negligibly small.

After the introduction of the pyrite electrode to the solution the rest potential of this electrode was registered for some time, until it stabilized. Then impedance spectrum at the rest potential was measured (usually three spectra one after the other were measured to check the stability of the system). All potentials in that work are quoted versus standard hydrogen electrode – when converting the potentials to SHE the potential of  $0.242$  for SCE was assumed. All measurements were performed at the constant temperature ( $25^\circ C$ ) box serving at the same time as a Faraday cage, in the dark to prevent the influence of light on the behavior of pyrite electrodes.

## RESULTS AND DISCUSSION

Most of the experiments were performed in the solution of the pH 1.85 and the concentration of the  $Fe^{2+}$  ions of  $0.5 \text{ mol dm}^{-3}$ .

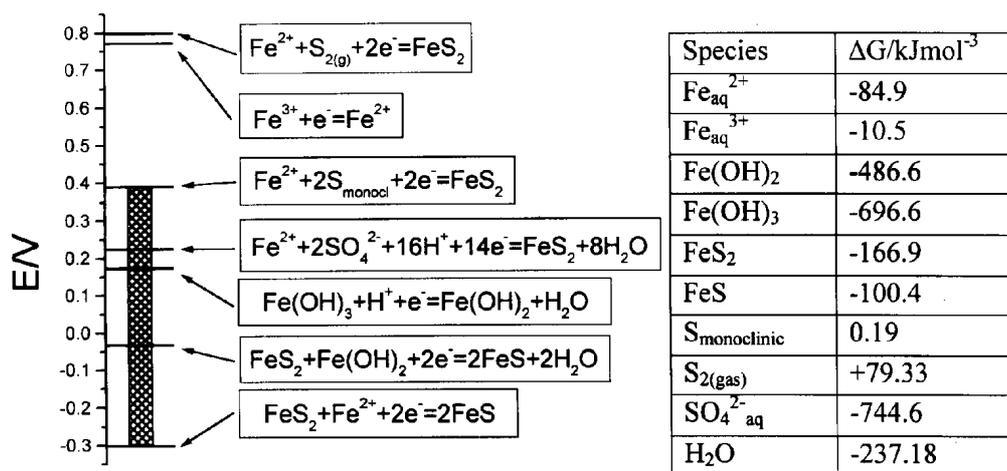


Figure 1. The potentials of different reactions, which may occur at the pyrite surface in the solution of iron (II), sulfate at the concentration of  $0.5 \text{ mol dm}^{-3}$  and pH 1.85. Table shows the values of free energy of formation for the species participating in the reaction

The equilibrium potentials of the reactions that may occur at the pyrite surface in that solution are collected in figure 1. It is to be seen that between the potential of the most probable reaction of pyrite dissolution (reaction 3) and the reaction of pyrite reduction to pyrrhotite (reaction 4) there is about  $0.7$  V difference. However, if iron hydroxides (or hydrated oxides) are present at the surface they may react in that potential range. Indeed, if freshly polished electrode was cycled in pure base

electrolyte solution, voltammetric maxima were observed in that range of potentials (Fig. 2), in accordance with the literature (Conway et al., 1980, Hamilton and Woods, 1981, Mishra and Osseo-Asare, 1988, Ramprakash et al., 1991). Note that the potentials of mentioned reactions do not depend on the presence of  $\text{Fe}^{2+}$  in solution - see Fig.1. However, when the electrode was introduced to the solution of  $\text{FeSO}_4$  and kept there for several hours the shape of the voltammogram changed (see Fig. 3).

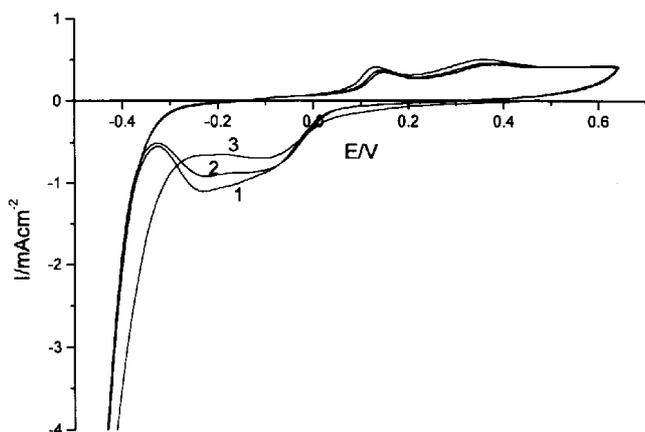


Figure 2. Cyclic voltammogram (first three consecutive cycles) for the Huanzala pyrite in  $0.5 \text{ mol dm}^{-3}$   $\text{Na}_2\text{SO}_4$  solution of pH 1.85. Potential sweep rate  $50 \text{ mV s}^{-1}$

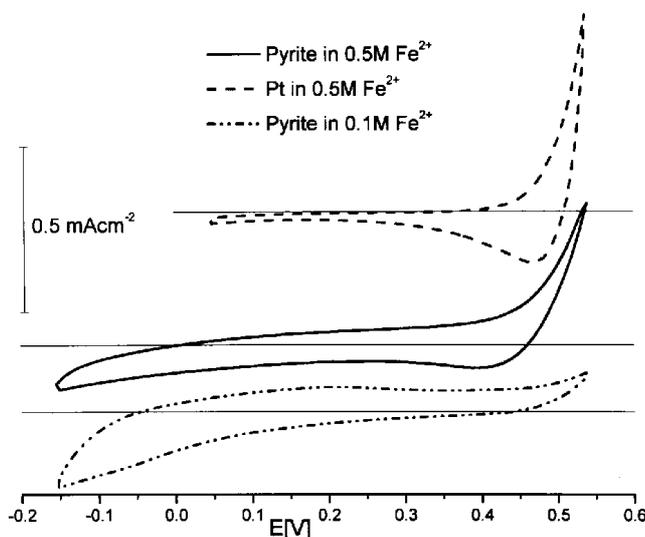


Figure 3. Cyclic voltammograms of the Huanzala pyrite in the solution of  $0.5 \text{ mol dm}^{-3}$  and  $0.1 \text{ mol dm}^{-3}$   $\text{FeSO}_4$  solution ( $0.5 \text{ mol dm}^{-3}$   $\text{Na}_2\text{SO}_4$  solution of pH 1.85 as a base electrolyte) and of Pt electrode in  $0.5 \text{ mol dm}^{-3}$   $\text{FeSO}_4$  solution ( $0.5 \text{ mol dm}^{-3}$   $\text{Na}_2\text{SO}_4$  solution of pH=1.85 as a base electrolyte). Potential sweep rate  $50 \text{ mV s}^{-1}$

The voltammetric maxima, which were ascribed to the redox transformations of surface hydroxides, disappeared (note however that the pyrite electrode in the  $0.1 \text{ mol dm}^{-3}$  solution still shows weak peaks in that region). Similar effect was observed by Bunges and Tributsch (1997) after etching of the pyrite electrode in sulfuric acid and

ascribed to the removal of the surface hydroxides. However only in the case of 0.5 mol dm<sup>-3</sup> FeSO<sub>4</sub> solution the potential stabilized close to the potential expected for the reaction of pyrite decomposition to elemental sulfur. For six experiments with six different electrodes potential stabilized between +0.19 and +0.37 V. It is to be seen in the figure 3 that the reaction of the oxidation of divalent iron in solution starts at the potential far from the equilibrium potential of the reaction  $Fe^{2+} = Fe^{3+} + e^{-}$ . This is the consequence of the relatively high exchange current density (ECD) for that reaction. Thus, the proper estimation of the ECD for reaction 5 might be made only if the measurement is performed at the potential sufficiently far from the equilibrium potential of the reaction  $Fe^{2+} = Fe^{3+} + e^{-}$  and if trivalent iron is very carefully removed from the solution.

For a series of 10 experiments on 6 different pyrite electrodes with 0.1 mol dm<sup>-3</sup> FeSO<sub>4</sub> solution the potential stabilized in the range of 0.35 – 0.5 V i.e. higher than expected for reaction (3) and higher than in the case of 0.5 mol dm<sup>-3</sup> FeSO<sub>4</sub> solution.

Note further that due to the inaccuracy of the data on free energy of formation of the considered species the equilibrium potential of any of the reactions may be known with only limited confidence. For the  $E^0$  of the reaction  $Fe^{2+} + 2e^{-} = Fe^0$  Heusler (1985) gives the value of  $-0.44 \pm 0.04$ . Similar range of confidence may be expected for any reaction in which  $Fe^{2+}$  ions participate.

Taking into account that the thermodynamic data for pyrite and sulfur may be also charged with some error, the potentials attained by pyrite electrodes in the 0.5 mol dm<sup>-3</sup> FeSO<sub>4</sub> solution may be close to the equilibrium potential of reaction 3. The potentials observed in the case of 0.1 mol dm<sup>-3</sup> FeSO<sub>4</sub> solutions were evidently too high (potential in 0.1 mol dm<sup>-3</sup> solution should be lower than the potential in 0.5 mol dm<sup>-3</sup> solution) if the composition of the mineral surface is the same. In one experiment performed in 0.5 mol dm<sup>-3</sup> FeSO<sub>4</sub> solution, after the stabilization of the potential and acquisition of the impedance spectrum the electrode was polarized in anodic direction to +0.44, +0.54, +0.64 and +0.74 V consecutively, for 100 s each time. Note that due to the presence of 0.5 mol dm<sup>-3</sup> FeSO<sub>4</sub> most of the charge was consumed in the reaction  $Fe^{2+} = Fe^{3+} + e^{-}$ , but some elemental sulfur might be formed at the surface too.

After each polarization the change of the rest potential in time was observed. The stabilization of the rest potential after the polarization to +0.74 V is presented in figure 4. It may be seen that there was no arrest on the curve at the potential of the reaction (3). It must however be remembered, that the freshly deposited sulfur is very reactive and as long as metallic iron is present in the system the elemental sulfur may recombine with iron according to the reaction  $Fe^0 + S^0 = FeS$  which is thermodynamically favorable. Naturally there must be a soluble redox mediator in the solution. Note also that the solution was all the time saturated with hydrogen (due to slow evolution of hydrogen on iron), that hydrogen may also reduce sulfur to

hydrogen sulfide. If no sulfur is present at the surface of the electrode, the pyrite electrode potential may attain practically any value within the range between the potential of reaction 3 and 4, depending on the exact stoichiometry of the surface.

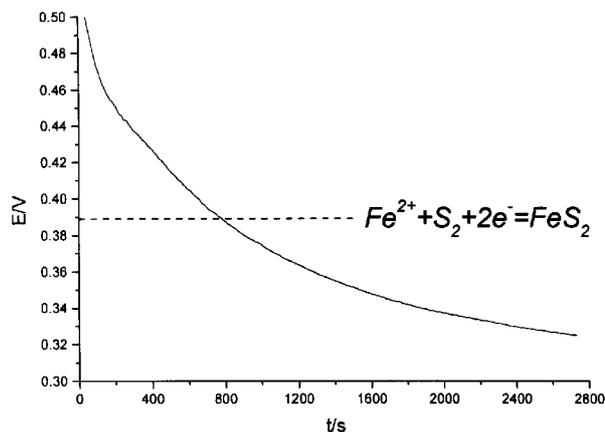


Figure 4. The change of the potential of the Huanzala pyrite electrode in the solution of  $0.5 \text{ mol dm}^{-3} \text{ FeSO}_4$  ( $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  solution of pH 1.85 as a base electrolyte), after the polarization to  $+0.74 \text{ V}$

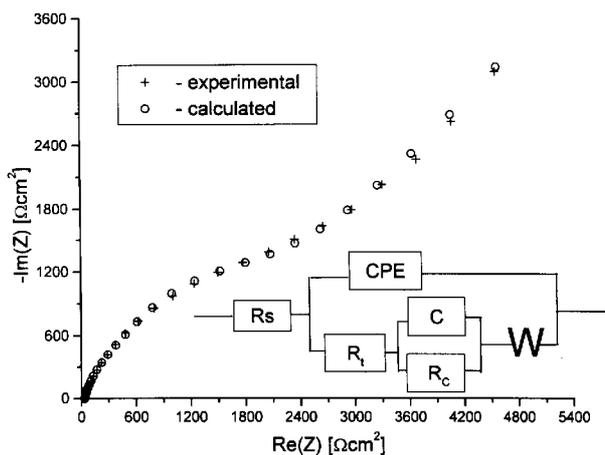


Figure 5. Impedance spectrum measured on Huanzala pyrite electrode in the solution of  $0.5 \text{ mol dm}^{-3} \text{ FeSO}_4$  ( $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  solution of pH 1.85 as a base electrolyte). + - measured points. o - impedance values for the EEC showed in figure and the parameters of EEC obtained by least-square fitting

The example of the impedance spectrum measured in the  $0.5 \text{ mol dm}^{-3} \text{ FeSO}_4$  solution at the rest potential is presented in Figure 5. Similar spectra were obtained in other experiments with the pyrite electrodes in the solutions of iron (II) sulfate. The key step in the interpretation of the impedance data is the selection of the proper EEC. The EEC shown in Fig.5 was assumed in the calculations. In that EEC  $R_s$  is the resistance of the electrode and the electrolyte,  $R_t$  is the charge-transfer resistance of the Faradaic reaction occurring at the surface, CPE (constant phase element) stands for the impedance of the electrical double layer at the interface pyrite/solution, C and  $R_c$  are connected with the capacitance of the surface states and W represent the diffusion (Warburg) impedance. The detailed discussion of the EEC for the phase boundary

semiconductor – electrolyte is out of scope of this paper so only the parameters influencing the dynamics of the exchange of  $Fe^{2+}$  ions between the surface and the solution will be discussed. Exhaustive discussion of the EECs of the boundary pyrite/solution may be found, for example, in the paper of Pang (1990).

Charge transfer resistance  $R_t$  may be associated with reaction (5). For the samples investigated in  $0.5 \text{ mol dm}^{-3} \text{ FeSO}_4$  solution the measured  $R_t$  values ranged between 950 and  $1500 \text{ } \Omega \text{ cm}^2$ , except one sample for which the value of  $350 \text{ } \Omega \text{ cm}^2$  was obtained, but in that case the fit of the EEC parameters to the measured data was much worse than in the other cases. The exchange current density for reaction (5) calculated from the formula:

$$i = \frac{RT}{2F} \frac{1}{R_t} \quad (6)$$

was between 8 and  $15 \text{ } \mu\text{A cm}^{-2}$  (except the lastly mentioned electrode). It means that every  $Fe^{2+}$  ion in the surface of pyrite exchanges place with a  $Fe^{2+}$  ion from the solution approximately one time per 5 seconds. This exchange current density was rather low. For non-stoichiometric cuprous sulfide electrode two of the present authors (Nowak and Pomianowski, 1985) estimated the ECD in  $1 \text{ mol dm}^{-3} \text{ CuSO}_4$  solution to be about  $100 \text{ mA cm}^{-2}$ . Warburg constants for the measured pyrite samples ranged between 300 and  $3900 \text{ } \Omega \text{ s}^{-1/2} \text{ cm}^2$  which gives the diffusion coefficient for iron in pyrite (the diffusion of  $Fe^{2+}$  ions in solution was orders of magnitudes faster) between  $2 \cdot 10^{-14}$  and  $1 \cdot 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ , assuming that every Fe atom in pyrite participates in the diffusion process. There is practically no data on diffusion in solids at room temperature, but this value seems to be too high. On the other hand there might be so-called accelerated diffusion paths in the solid body, which usually allow relatively fast diffusion to take place, even at the room temperature.

The capacitance of the electrical double layer at the surface of pyrite electrodes in  $0.5 \text{ mol dm}^{-3} \text{ FeSO}_4$  solution was calculated to be between 10 and  $25 \text{ } \mu\text{Fcm}^{-2}$  (this value comprises mainly the capacitance of the space charge layer in semiconducting pyrite). Taking into account very rough surface, polished on emery papers, (and hence the relatively high surface roughness factor) this values seems to be reliable. Also the value of capacitance connected with the surface states was obtained in quite good agreement with the prediction of Bronold et al. (1994), based on theoretical calculations. That increases the confidence to the correctness of the choice of the EEC for the investigated interface.

As was already stated ten experiments were performed on  $0.1 \text{ mol dm}^{-3} \text{ FeSO}_4$  solution. Only in one case the potential of pyrite electrode was below the potential of reaction (3). Evidently, it means that the measured potential was a mixed (corrosion), not equilibrium potential and the measured current was not the exchange current but rather the corrosion current. Indeed, for some electrodes the  $R_t$  values much lower than in the case of  $0.5 \text{ mol dm}^{-3}$  solution (of the order of  $800 \text{ } \Omega \text{ cm}^2$ ) were observed.

Note the potential attained by these electrodes is situated in the range where divalent iron starts to be oxidized. Further, the traces of the surface oxides were discernible on the voltammograms; these surface oxides may produce parasitic currents due to the reactions of their redox transformations.

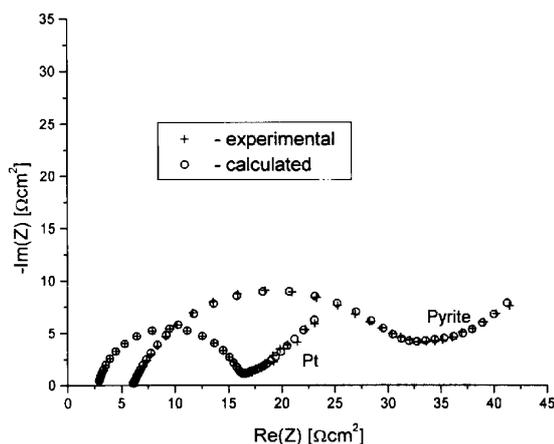


Figure 6. Impedance spectra of pyrite and platinum electrodes in the solution of the composition:  $0.5 \text{ mol dm}^{-3} \text{FeSO}_4 + 0.25 \text{ mol dm}^{-3} \text{Fe}_2(\text{SO}_4)_3, 0.5 \text{ mol dm}^{-3} \text{Na}_2\text{SO}_4$  solution of  $\text{pH}=1.85$  as a base electrolyte

It should be stated that it was not the low free carriers concentration within the semiconductor pyrite which caused that so low current flow in the experiments in  $\text{FeSO}_4$  solutions. When a redox couple, able to exchange the electrons with the electrode was present in the solution, quite high current flow through the electrode surface. Figure 6 presents the comparison of the impedance spectra made on platinum and pyrite electrodes (Ural pyrite) in the same solution ( $0.5 \text{ mol dm}^{-3} \text{FeSO}_4 + 0.25 \text{ mol dm}^{-3} \text{Fe}_2(\text{SO}_4)_3, 0.5 \text{ mol dm}^{-3} \text{Na}_2\text{SO}_4$  solution of  $\text{pH} 1.85$  as a base electrolyte). It is to be seen that the pyrite electrode shows  $R_t$  for the reaction  $\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$  only about 2 times higher than Pt electrode (which may be estimated from the diameters of the activation semicircles in both cases). It means that the ECD for pyrite electrode is only about two times lower than for platinum, which is known to be the best electrode material. This is in accordance with the electronic structure of the pyrite surface proposed by Bronold et al. (1994). These authors state that due to specific electronic situation there is a very high density of surface states (about  $5.5 \times 10^{14} \text{ cm}^{-2}$ ) at the pyrite surface. Due to this situation the Fermi level is pinned at a specific position at the surface and the pyrite electrode shows the behavior similar to metal electrodes.

## CONCLUSIONS

Despite the fact that both iron(III) as well as iron(II) sulfates are well soluble in water, the surface of the pyrite electrode always contain some hydrated iron oxides at the surface even in acidic solutions. Surface iron oxides govern the behavior of pyrite electrode at moderately cathodic potentials and moderately anodic potentials. These

oxides may be removed from the surface by equilibration of the electrode with the solution of iron (II) sulfate of high concentration, being in turns in contact with metallic iron. Only in the  $\text{FeSO}_4$  solutions of the highest concentration used (practically close to saturation) it was possible to measure the exchange current density for the reaction  $\text{Fe}_{1+y}\text{S}_2 = \text{Fe}_{1+y-x}\text{S}_2 + x\text{Fe}^{2+} + 2x\text{e}^-$  in the case of natural pyrite electrodes.

In the solutions of the lower concentration rather the corrosion currents were measured. The measured ECD was of the order of  $10 \mu\text{Acm}^{-2}$ , orders of magnitude lower than, for example, in the case of cuprous sulfide electrode. Even this value may be overestimated, because for any electrode there are always some parasitic currents flowing through the electrode surface (due to, for example, impurities present in the solution). So, it may be stated that the ECD for the above written reaction is very low. It means that when assessing the mechanism for pyrite oxidation in aqueous solution the non-electrochemical path must be taken into account. This non-electrochemical path might be either the direct attack of the oxidant on the surface or the so-called dissolution-precipitation mechanism. In the later case sulfide first dissolve, than the components of the sulfide undergo the oxidation.

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Na podstawie pomiarów impedancji elektrod piritowych w roztworach siarczany żelaza (II) oceniono wartość gęstości prądu wymiany dla reakcji:  $Fe_{1+y}S_2 = Fe_{1+y-x}S_2 + xFe^{2+} + 2xe^-$ . Dla pięciu elektrod piritowych w roztworze siarczany żelaza (II) o stężeniu  $0,5 \text{ mol dm}^{-3}$ , przy potencjale zbliżonym do potencjału równowagowego reakcji:  $FeS_2 = Fe^{2+} + 2S^0 + 2e^-$ , wyznaczono prąd wymiany pomiędzy 8 i  $15 \mu\text{A cm}^2$ . Niska wartość prądu wymiany powoduje, że elektroda piritowa w roztworach siarczany żelaza (II) nie osiąga wartości równowagowych, to znaczy wartości w obszarze termodynamicznej stabilności elektrody, z wyjątkiem najbardziej stężonych i dobrze odtlenionych roztworów. W przypadku roztworów siarczany żelaza (II) o stężeniu mniejszym niż  $0,5 \text{ mol dm}^{-3}$  potencjał spoczynkowy elektrody przyjmuje wartości poza zakresem termodynamicznej stabilności, co oznacza że mierzony potencjał jest potencjałem korozyjnym (mieszanym) a nie potencjałem równowagowym.