SEM, EDX and EIS study of an electrochemically modified electrode surface of natural enargite (Cu$_3$AsS$_4$)

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Abstract

Enargite electrodes, made from mineral originating in the ‘Salvador’ mine (Chañaral, Chile), have been studied using SEM, EDX, CV and EIS in an alkaline solution for a range of different potentials in the positive sweep direction (PSD) and negative sweep direction (NSD). The results of SEM and EDX have shown that the principal changes in morphology and chemical composition take place on the surface of the electrode for oxidation potentials close to the value that corresponds to the most intense peak in the PSD, where there is clearly formation of a layer of oxidised material with areas of morphology which are irregular and high in oxygen content. These results are in accordance with the findings from XPS studies published previously. The charge transfer resistance and the resistance of the anodic layer of the electrode were determined by EIS measurements; the values depend heavily on the applied potential in the PSD or NSD. These changes are related to the changes on the surface of the electrode studied by SEM and EDX © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Enargite; EIS; SEM; EDX; Mineral electrode; Copper minerals

1. Introduction

Enargite (Cu$_3$AsS$_4$), a metal sulphide which is frequently found as an impurity in copper ores, is a mineral that corresponds to a semiconductor species of type $A_3B^5C_4^2$ with p-type conductivity [1,2]. Its crystal structure is orthorhombic, based on wurtzite ($\alpha$-ZnS) [3]. The values of the crystal lattice parameters $a$, $b$ and $c$ are 6.47, 7.44 and 6.19 Å respectively [4]. Each As and Cu atom is surrounded by four S atoms. Further, each S atom is centred in a tetrahedron formed from one As atom and three Cu atoms. This results in the appearance of discrete As$_4$S$_4$ groups in the enargite structure. Given the tetrahedral fashion in which the atoms are arranged, one can expect effects due to strong covalent bonds and highly delocalized holes. The main impurities in natural enargite are iron and antimony, but lead and silver can also be present to some extent [5].

Enargite is a mineral which gives rise to significant arsenic pollution during the industrial procedure of copper mining; moreover, it is necessary to eliminate traces of arsenic from the metal after processing [6,7]. Many copper sulphide ores in Chile contain enargite and it would thus be useful to improve the separation of enargite from the other copper sulphide minerals during the initial processing steps.

The behaviour of the mineral particle during the flotation process is affected by its surface properties and its interaction with the electrolyte. During flotation, ground mineral is placed in a basic solution containing a collector (usually a xanthate) and molecular oxygen (air bubbling). In this process the surface of the mineral undergoes considerable changes in its chemical composition due to interaction with the electrolyte. On the mineral surface there are redox reactions, adsorption of molecules, and in general, diverse electrochemical processes which modify the surface to such an extent that it can be considered as a heterogeneous film.
of modified mineral which is quite different from the substrate. These compositional changes on the surface alter profoundly the electrical properties at the mineral | electrolyte interface. The surface of many mineral particles, having been made hydrophobic by collector adsorption, can cause air bubbles to adhere. The surface processes leading to flotation are very complex and depend on the change in chemical composition and the reactivity of the mineral surface for different applied potentials in a basic solution as in the industrial flotation process. These changes in the chemical composition and reactivity of the mineral surface are very important because the chemisorbed collectors are the chemical species responsible for flotation.

Traditional electrochemical methodology (cyclic voltammetry, CV, and, more recently, electrochemical impedance spectroscopy, EIS) permit the study of electrical interactions between the electrode and the electrolyte, and how these vary with different oxidation potentials. Thus, EIS allows a tentative model of the electrode–electrolyte interaction via equivalent electrochemical circuits composed of capacitance, resistance, and impedance of diffusion whose values depend on the chemical composition of the electrode surface. However, these methods do not allow the morphological or chemical composition alterations, which in turn give rise to the electrochemical processes measured as a function of the applied potential, to be established. On the other hand, other analytical techniques such as SEM, EDX and XPS can be used to give complementary information about the nature of the electrode surface. But the use of SEM, EDX, and XPS [8] in the study of the electrode surface modifications as a function of the applied oxidation potential requires the construction of an inert atmosphere chamber. The electrochemical processes can be carried out in such a chamber and then the electrode is transferred for analysis into the XPS, SEM, or EDX chambers, thus allowing contact of the electrode surface with the atmosphere and consequent chemical composition modifications of the electrode. Hence, in a previous publication, XPS studies were performed quasi in situ, employing a controlled inert atmosphere chamber coupled to the XPS chamber, allowing the oxidation states of the different elements within the enargite and the electrode surface throughout the voltammogram to be studied [9].

The aim of the current work is twofold. Firstly, we applied SEM and EDX to the study of changes of a natural enargite electrode surface during cyclic voltammetry and contrasted the results with results from a previous study using XPS [9]. Secondly, these XPS results were related to results obtained with SEM and EDX with the changes in the electrochemical parameters as determined by EIS measurements for the same potential values applied throughout the cycle of the voltammogram. To this end, the experiments evolving SEM, EDX and EIS were carried out for the most significant potentials of the voltammogram.

2. Experimental

The working electrode is natural enargite \((\text{Cu}_3\text{AsS}_4)\) provided by the company ‘Salvador’ (Chañaral, Chile); its crystalline structure has been determined by X-ray diffraction. The sample was placed on epoxy resin with the area of electrode exposed to the electrolyte being 0.2 cm². The electrode was connected to copper wire with In–Ga. The auxiliary electrode was graphite and the reference electrode was a saturated calomel electrode (SCE). Before each measurement, i.e. for each applied potential, a fresh electrode surface was prepared by wet abrading with 600-grade silicon carbide paper and then rinsing with deoxygenated deionised water. Finally, a fine polish was achieved with an alumina suspension of first 0.3 μm and then 0.05 μm particle size, both from Buehler. After electrochemical treatment each electrode surface was cleaned by rinsing with water before SEM and EDX analysis. The electrolyte solution was prepared with disodium tetraborate decahydrate (borax) from Merck (EWG-Nr. 215-540-4) to 0.05 M in deoxygenated deionised and, by heat treatment, decarbonated water, thus obtaining a constant ionic strength of 0.2 at pH 9.2. Voltammetry measurements were performed with a computer controlled Solartron El 1286 by means of a specialized program and connected to the electrochemical cell via a 3 mm diameter copper feed-through into the glove box. The d.c. potential range used was from \(-0.15\) to \(+0.6\) V vs. SCE. The scan rate for voltammetry was 5 mV s⁻¹ with the limits \(-0.15\) V to \(+0.6\) V vs. SCE, in the positive sweep direction (PSD) and \(+0.6\) V to \(-0.85\) V vs. SCE, in the negative sweep direction (NSD). For the voltammogram, the points of study for surface modification were \(-150\) mV (point 0), \(-50\) mV (point 1), \(+200\) mV (point 2), and \(+500\) mV vs. SCE (point 3), in the PSD, and \(+200\) mV (point 4), \(-150\) mV (point 5), \(-600\) mV (point 6), and \(-800\) mV vs. SCE (point 7) in the NSD. Each potential was applied to the electrode for at least 400 s or, if necessary, until steady state current intensity was reached. Impedance data were recorded with a Solartron 1255 frequency response analyser. For all impedance measurements, the Solartron FRA sine wave output was superimposed on an applied d.c. bias from the Solartron EI 1286. The FRA and the electrochemical interface (EI) were both computer controlled by means of a specialised program. A.c. measurements were taken for the frequency range from 10 mHz to 10 kHz for different d.c. applied potentials and an a.c. potential of 0.01 V rms. EIS measurement were carried out for each point of study (see above). All measurements were carried out at 25°C.
SEM micrographs and EDX spectra were obtained with a Jeol JSM 6400 scanning electron microscope equipped with a Link analytical system. The electron energy used was 20 keV. For our study we used a glove box filled with Ar gas (99.999%) and coupled to the SEM chamber for both the electrochemical treatment and for the EIS experiments. In this way, the SEM and EDX analyses were carried out for the same points as the EIS experiments without changes in the chemical composition of the electrode surface.

3. Results and discussion

3.1. Cyclic voltammetry

Previous voltammetry experiments have been done to determine the main peak currents. Those peaks are associated with redox processes in the electrode surface. Fig. 1 shows the voltammetry curve \( I/E \) in a borate buffer solution of pH 9.2. In the voltammogram, an anodic current (peak A, charge of 8.69 mC cm\(^{-2}\)) can be seen at 0.1 V vs. SCE and another anodic current (peak B, charge of 10.13 mC cm\(^{-2}\)) at 0.6 V vs. SCE, both in the PSD. Afterwards in the reverse scan, two different peaks denoted peak C (charge of 4.96 mC cm\(^{-2}\)) at −0.1 V, and D (charge of 5.63 mC cm\(^{-2}\)) at −0.65 V, all vs. SCE, are found [7].

In previous work, some of our team studied in detail the voltammetric behaviour of enargite and the possible electrochemical reactions that were taking place on the enargite surface on being subjected to varying potential [7]. Furthermore, others from our team, in a different previous work [9], used XPS to study the changes in oxidation state of the enargite elements for the same points previously mentioned above. For each applied potential, the atomic concentrations of all atoms were calculated as percentages from XPS spectra. From point 0 (−50 mV vs. SCE) to point 2 (+200 mV vs. SCE), passing peak A, there is a slow continuous decrease in the concentration of Cu with respect to As and S on the electrode surface, and a slight increase in S concentration with respect to As. For peak B (+500 mV vs. SCE), the surface of the electrode changed entirely due to its total oxidation, and CuO, As\(_2\)O\(_5\), As\(_2\)O\(_3\), CuSO\(_4\) and the corresponding hydroxide were found. The concentration of Cu and As also suffered a notable increase along with a decrease in S. In the case of sulphur there is a modification in binding energy due to the formation of polysulphides in the superficial enargite structure [10,11]. Polysulphides are well-known unbranched sulphur chains, which can be considered the anion of the weak di-basic acid \( \text{H–S–S} \). At 200 mV (now in the NSD) these oxide, hydroxide and sulphate species, except the sulphides, disappear and we return to a situation very similar to that before peak B (in the PSD). This shows clearly that the oxidised species formed on the surface of the electrode are only stable when they have high oxidation potentials applied to them. Moreover, after peak B, at +200 mV vs. SCE in the NSD, there is a large decrease in the concentration of Cu, which at more negative potential increases, little by little, until it reaches, at −800 mV vs. SCE, a concentration almost the same as before the electrochemical treatment.

3.2. SEM and EDX analysis

The surface of the polished electrode appears as a flat surface with small holes and bright spots, which occupy approximately 3% of the surface area of the electrode (Fig. 2a). The analysis with EDX of the surface composition shows it to be Cu\(_3\)AsS\(_3\), very close to the stoicheometry of enargite (Fig. 3a), which is in agreement with results obtained using XPS for a fractured enargite surface [9]. Through EDX analysis, it was determined that the bright islands are small pieces of quartz encrusted in the surface, whilst the small white spots are quartz particles (SiO\(_2\)) which originate from the quartz islands encrusted in the mineral which have been scratched during polishing and thus are dispersed across the whole surface. The presence of quartz has also been detected by XPS [9]. At point 1, (−50 mV vs. SCE in the PSD) (not shown), the small bright spots have virtually disappeared, resulting in no noticeable changes in the chemical composition. At point 2 (+200 mV vs. SCE in the PSD) (not shown) no significant changes are observed with respect to the last point. At point 3 (Fig. 2b; +500 mV vs. SCE in the PSD), in the SEM image, the surface appears to be more irregular with widespread bright spots, some of them form agglomerations along lines which appear as grain size borders. In addition, some scratch lines from polishing

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![Volammogram for enargite electrode in a borate buffer solution (pH 9.2). Point 0 (V_{dc} = −150 mV in PSD); point 1 (V_{dc} = −50 mV in PSD); point 2 (V_{dc} = +200 mV in PSD); point 3 (V_{dc} = +500 mV in PSD); point 4 (V_{dc} = +200 mV in NSD); point 5 (V_{dc} = −150 mV in NSD); point 6 (V_{dc} = −600 mV in NSD); point 7 (V_{dc} = −800 mV in NSD). All V_{dc} are versus SCE.](image-url)
can be seen diagonally across the microphotograph. The quartz particles have disappeared on the electrode surface due to the repeated polishing processes and rinsing with water from point 0 to point 3. The composition of the surface layer, obtained from EDX analysis (Fig. 3b), is similar to that of enargite and is the same for darker and lighter areas. On the other hand, the bright protrusions have a characteristically high oxygen presence (26.5%) and a decrease in the concentration of Cu (30%), As (9.3%), and S (34%) (Fig. 3c). These points can be considered as points of high oxide concentration even though oxides can also be found in other parts of the surface. These results are consistent with those obtained previously with XPS in which it is clear that the surface of the electrode is totally oxidised. One has to take into account that the sensitivity of XPS is very different to that of EDX measurement. The X-rays sampled in EDX originate from a depth of about 5000 Å at 20 keV. Thus the surface measurements are heavily influenced by the substrate and not...
only the uppermost atomic layers are seen, as is the case with XPS. These results allow us to affirm that the electrode surface is composed of a very superficial heterogeneous layer of oxidised material from which protrude islands formed from grains of oxide, hydroxide and sulphate material. At point 4 (+200 mV vs. SCE, NSD) (Fig. 2c) bright spots also appear, but they are very dispersed on the electrode surface and do not form agglomerations. Also polishing scratches can be seen. EDX analysis of the surface of the electrode shows a stoichiometry very similar to that of the previous point; again the bright spots present an elevated concentration of oxygen (41.9%) and a decrease in the concentration of the other elements (Cu, As, and S). In this case, these changes in the oxygen concentration cannot be attributed to the oxidation of copper or sulphur in the enargite since from XPS data it is clear that no oxide, hydroxide and sulphate species remain at the electrode surface (see figure 2 and the table of Ref. [9]). These bright spots with high oxygen content are possibly due to the residual Al₂O₃ from polishing, and were also detected in some cases by XPS. Further, it is important to stress that the surface area coverage of these spots is greatly inferior to the surface area coverage of the agglomerations of bright spots as seen at the previous potential. At the remaining points there are no significant changes either in the SEM photographs or in the EDX spectra, except at points 6 and 7 which correspond to the potentials of −600 and −800 mV vs. SCE in the NSD, respectively and represent the limit of reduction. In the first of these (point 6, Fig. 2d), which corresponds to the potential before peak D of the voltammogram, a large number of small dark stains can be seen, and sometimes also irregular white stains, larger than those that appeared in the photographs for points 3 and 4. EDX analysis of the dark stains revealed no differences with respect to the general surface composition, showing a stoichiometry very similar to that of enargite. The bright spots show a high concentration of oxygen (35%), the origin of which is attributed to surface contamination (Fig. 3d). The last point studied, point 7, shows a clean surface with only a few residual encrustations of aluminium oxide, and on examination in EDX, the surface stoichiometry was very similar to that in the initial cycle.

3.3. EIS

The EIS measurements were taken at the same points as for SEM and EDX measurements. Fig. 4 shows the Nyquist plots, Fig. 5 the Bode plots for the phase angle and Fig. 6 the equivalent circuits. Experimental data have been fitted to equivalent circuits by a non-linear method [12]. Fitting to the equivalent circuits was carried out based on criteria of simplicity and electrochemical interpretation [13]; the fits represent an approach to the description of the electrochemical processes at the electrode | electrolyte interface, and any models derived from them are tentative. The circuit for the first point of measurement, point 0 (\( V_{dc} = -150 \) mV; Fig. 4a, Fig. 5a and Fig. 6a), corresponds to three relaxation processes; \( R_e \) is the resistance of the electrolyte and other ohmic resistance, \( R_a \) is the charge transfer resistance, \( Q_d \) and \( Q_{di} \) refer to the processes on the electrode surface where \( Q_{di} \) represents the double layer in the electrode | electrolyte interface. \( Q_{di} \) and \( Q_{di} \) were modelled by a constant phase element (CPE) [13]. The constant phase element is a distributed element defined as \( Q = 1/Kp^n \), \( 0 < n \leq 1 \). In this expression, \( n \) is a dimensionless number, \( K \) is a constant whose dimension is \( F \ s^{-1} \ cm^{-2} \) and \( p = j\omega \) with \( \omega = 2\pi f \). \( Q \) is equivalent to the impedance having a capacitance of \( C = K(2\pi f)^n \), that is, the CPE behaves as a capacitance which varies with the frequency. This modification to an ideal capacitance has already been explained by distribution effects [14], porosity [15], fractal geometry [16] or more recently, by distribution of interfacial capacitances [17,18]. The circuit corresponding to \( V_{dc} = -50 \) mV vs. SCE in the anodic sense, point 1, is of a Randles type (Fig. 4b, Fig. 5b and Fig. 6b). The Randles circuit describes the response of a single-step charge transfer process with diffusion [19]. In this circuit \( R_{ct} \) is associated with the charge transfer resistance of the initial enargite oxidation stage or at the Cu-depleted mineral phase [7]. The Warburg impedance, \( W \), accounts for the transport of released copper ions from the mineral matrix leaving a Cu-depleted phase whose composition changes to a structure like AsS₄ or Cu(₃₋ₓ)AsS₄. The constant phase element, \( Q_{di} \), corresponds to a double layer. For all higher potentials applied in the PSD, we obtain the same type of equivalent circuit, Fig. 6c. This circuit corresponds to two faradaic relaxation processes; \( R_e \) is the resistance of the electrolyte and other ohmic resistance, \( R_a \) the anodic layer resistance, \( R_{ct} \) the charge transfer resistance, \( Q_{di} \) refers to an irregular double layer capacitance \( (n \neq 1) \) [21]. \( Q_i \) corresponds to the capacitance of an irregular layer coating \( (n \neq 1) \) [21]. This circuit is often used to represent an imperfectly covered electrode [20,21]. For potentials applied in the NSD, between +200 mV and −150 mV vs. SCE, the equivalent circuits change to a modified Randles one in which the impedance \( W \) is substituted by a CPE (Fig. 6d). Furthermore, the values of charge transfer resistance are very similar to each other. For the potential \( V_{dc} = -600 \) mV vs. SCE, which corresponds to a potential close to the last cathodic peak, the circuit displays changes to the circuit shown in Fig. 6c. This last circuit corresponds to a double faradaic relaxation process in the surface electrode similar to its equivalent at point 2 (+200 mV vs. SCE in the PSD). This change is accompanied by a strong decrease in the layer resistance. Nevertheless, the resistance \( R_{ct} \) merely changes.
Fig. 4. Nyquist plots for complex impedance for different points: (a) $V_{dc} = -150$ mV vs. SCE; (b) $V_{dc} = -50$ mV vs. SCE in PSD; (c) $V_{dc} = +200$ mV vs. SCE in PSD; (d) $V_{dc} = +500$ mV vs. SCE in PSD; (e) $V_{dc} = +200$ mV vs. SCE in NSD; (f) $V_{dc} = -150$ mV vs. SCE in NSD; (g) $V_{dc} = -600$ mV vs. SCE in NSD.
Fig. 5. Bode plots for phase angle for different points: (a) $V_{dc} = -150$ mV vs. SCE; (b) $V_{dc} = -50$ mV vs. SCE in PSD; (c) $V_{dc} = +200$ mV vs. SCE in PSD; (d) $V_{dc} = +500$ mV vs. SCE in PSD; (e) $V_{dc} = +200$ mV vs. SCE in NSD; (f) $V_{dc} = -150$ mV vs. SCE in NSD; (g) $V_{dc} = -600$ mV vs. SCE in NSD.
Nyquist and Bode plots derived from the results obtained in positive cycling input (points 0, 1, 2 and 3) and negative cycling input (points 4, 5, 6 and 7) are very similar (Figs. 4 and 5). Nevertheless, a more detailed analysis of these results by means of equivalent circuits reveals that there are significant differences.

The main transformation in the characteristic parameters of the PSD section, Table 1, occurs at point 3 (+ 500 mV vs. SCE) where the charge transfer resistance is reduced to a fifth of the value of the previous point, therefore increasing the charge transfer; on the other hand, the surface resistance is reduced. These changes are attributed to the formation of a layer of oxidised material on the surface of the electrode, on which agglomerations of small islands appear, with a high concentration of oxygen. This transformation is due to the formation of CuO, As₂O₅, As₂O₃, CuSO₄ and their hydroxides, which modify the surface conductivity and the permittivity with respect to the initial surface electrode. The resulting electrode surface is heterogeneous in composition and morphology since these agglomerations of islands of high oxygen content form protrusions on a film of oxidised material for which reason we are prevented from obtaining the value of the resulting conductivity and permittivity of the corresponding compounds formed. However, the relatively high presence of CuO [9], which is also the compound with the highest conductivity, will explain at least the qualitative part of these changes. Moving on to the potentials in the NDS, this supposes a change in the type of equivalent circuit, the EIS data now being best represented by a modified Randles circuit. This difference means changing from a system characterised by processes on the electrode surface to another in which diffusion controlled charge transfer has more relevance. This behaviour agrees with the SEM and EDX results obtained. The almost total disappearance of oxidised enargite material means that we are in a very similar situation to the case of the initial potentials of the voltammogram from −50 mV vs. SCE in the PSD. Also, the presence of some very superficial agglomerations of bright spots, possibly formed from Al₂O₃, makes a heterogeneous surface, which explains the substitution of the Warburg impedance of the Randles circuit for a CPE, which would represent a non-homogeneity on the electrode surface. Fig. 7 shows a model for the different steps in the surface transformation during PSD. These irregularities are due to initial inhomogeneities of the enargite mineral at the electrode surface in step a, which have caused a surface selective oxidation process resulting in a partial covering of the surface by transformed material in step b, which grows on specific areas of the electrode surface over the oxidised surface in step c. If the potentials used in the NSD continue to be applied, we return to a circuit characterised by two relaxation processes, Fig. 6, since now the surface processes become more important again due to the increase in size of the zones of differing composition and morphology in the area around point d.

Table 1

<table>
<thead>
<tr>
<th>Potential (mV vs. SCE)</th>
<th>Rₛ/kΩ</th>
<th>10⁴Qₛ/Ω⁻¹ Hz⁻¹</th>
<th>n</th>
<th>Rₑ/kΩ</th>
<th>10⁴Qₑ/Ω⁻¹ Hz⁻¹</th>
<th>n</th>
<th>Rₛ/kΩ</th>
<th>10⁴Qₛ/Ω⁻¹ Hz⁻¹</th>
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<th>10⁴Qₑ/Ω⁻¹ Hz⁻¹</th>
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<tr>
<td>−150 PSD</td>
<td>0.158</td>
<td>0.4719</td>
<td>0.67</td>
<td>0.0442</td>
<td>44.89</td>
<td>0.1629</td>
<td>0.99</td>
<td>24.79</td>
<td>0.8076</td>
<td>0.57</td>
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<tr>
<td>−50 PSD</td>
<td>0.161</td>
<td>7.714</td>
<td>0.68</td>
<td>20.49</td>
<td>1.051</td>
<td>0.1629</td>
<td>0.48</td>
<td>0.87</td>
<td>1.495</td>
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<tr>
<td>200 PSD</td>
<td>0.158</td>
<td>0.3769</td>
<td>0.68</td>
<td>23.74</td>
<td>21.69</td>
<td>1.431</td>
<td>0.83</td>
<td>0.83</td>
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<td>0.87</td>
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<tr>
<td>500 PSD</td>
<td>0.168</td>
<td>0.2347</td>
<td>0.76</td>
<td>4.523</td>
<td>4.286</td>
<td>1.431</td>
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<td>0.83</td>
<td>1.495</td>
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<td>0.144</td>
<td>0.2141</td>
<td>0.80</td>
<td>5.457</td>
<td>2.149</td>
<td>0.40</td>
<td>0.40</td>
<td>0.40</td>
<td>1.495</td>
<td>0.87</td>
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<tr>
<td>−150 NSD</td>
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<td>0.62</td>
<td>2.543</td>
<td>4.241</td>
<td>0.38</td>
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<td>1.495</td>
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<tr>
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<td>1.495</td>
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Fig. 6. Equivalent circuits: (a) three relaxation processes; (b) Randles circuit; (c) two faradaic relaxation processes; (d) modified Randles circuit.

Fig. 7. Proposed model for surface changes.
4. Conclusions

The oxidation of enargite in an alkaline medium results in a modification of the morphology and chemical composition of the surface. The joint application of analytical (SEM, EDX, and XPS) and electrochemical (CV, EIS) techniques permits the relationship between morphological and compositional changes of the surface and changes in the most characteristic electrochemical parameters, as determined by EIS, to be established.

The measurements by SEM and EDX, performed at different potentials following the voltammogram, agree with the results obtained with XPS published in a previous study, and show clearly how the modification of the surface, as much morphologically as in chemical composition, results in a heterogeneous surface, with protrusions of differing chemical compositions and morphologies which are spread irregularly over the electrode surface. These islands contain a high concentration of oxygen, showing them to be centres of oxidation. These changes are greater in the case of potentials close to the peaks of the voltammogram. The transformations on the surface of the electrode cause changes in the kind of equivalent circuit that best represents the EIS data, changing from Randles circuits to circuits characteristic of partially covered electrode surfaces. Furthermore, the charge transfer resistance on the surface also shows a strong dependence on the potential considered on the voltammogram to which the SEM, EDX, and EIS measurements were subjected. Both resistances decrease greatly in the area around the last peak of the voltammogram in the PSD.

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