

Impedance Study During Anodic Oxidation of Native Galena in a Highly Concentrated Xanthate Solution

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Received: 5 October 2011 / *Accepted:* 11 November 2011 / *Published:* 1 December 2011

A double-layer capacitance and EIS studies on galena in absence and presence of sodium isopropyl xanthate at high concentrated solution in a wide range of polarization potentials is presented. A cyclic voltammetry study complements the EIS and double-layer capacitance data. The shape of the capacitance-potential curve as a function of the xanthate concentration evidences a large surface modification of the galena interface at high thiocollector concentrations. Potential Zero Charge (PZC) for the system at -0.31 V vs. SCE coincides with the oxidation and adsorption of xanthate (X^-) on the galena surface, determined from the capacitance-potential curves. The impedance spectrum for the system obtained in the presence of X^- (0.1 M) at the PZC show two time-constants associated to the oxidation and adsorption of X^- and the subsequent formation of dixanthogen (X_2) according to experimental results obtained and previous data published in the literature. EIS data at more positive potentials than PZC (+0.1 V, 0.2 V) show an inductive loop which is associated to a charge transfer processes which involves the reaction of the adsorbed intermediates $Pb(X)_2$ and $Pb(OH)_2$ with the consequent modification of the PbS-sodium isopropyl xanthate interface. These results provide new findings that contribute to a better understanding of the galena-xanthate interface at high xanthate concentrations.

Keywords: Galena, xanthate, PZC, EIS.

1. INTRODUCTION

The sulfide ores are the main source of several engineering metals, such as lead, copper and zinc the foremost lead ore is lead sulfide and galena [1]. Worldwide lead productions is steadily

grown with a global production of 4117 000 tonnes for the 2010, this represent an increment of 6% respect to 2009 [2].

From all the separation process flotation-depression is the most used procedure employed in commercial ore treatment plants to concentrate value minerals from gangue and other associated minerals. The flotation of sulfide minerals, with an ore complex composition has been extensively studied [3-7]. Nowadays, there is a consensus that flotation of galena involves the adsorption of thiocollectors on the surface, such as xanthates, which allow to obtaining lead concentrates until 60% [1]. Xanthate galena interactions involve the oxidation of the xanthate and its subsequent adsorption on galena [3].

Therefore, electrochemical techniques are suitable tools to further investigate and understand the flotation processes. In this vein, Woods carried out a pioneer work with the use of chronoamperometry technique; and demonstrated that the reaction of the thioccollector adsorption was an electrochemical oxidation, with the oxygen reduction reaction as a conjugated charge-balancing cathodic reaction [8]. After its works, other authors have performed electrochemical studies of galena immersed in xanthate solutions at different experimental conditions. Most of them have focused on the adsorption mechanisms and the electrochemical and semiconducting properties of minerals [1, 8-14]. However, there is still much uncertainty about how really the interactions between galena and xanthate take place.

In addition, there are other cyclic voltammetry studies of galena/xanthates interface under an inert atmosphere reported in the literature [1,9-11]. According to these studies, it is recognized that oxidation products of galena, such as PbS_2O_3 and $PbSO_4$, react with xanthates X^- to produce $Pb(X)_2$. A proposed mechanism for the $PbS-X$ reaction involves the adsorption of X^- , that can be either physical or chemical depending on the xanthate concentration [10]. Once the xanthate is adsorbed onto the galena surface, the subsequent formation of dixanthogen $(X)_2$ and $Pb(X)_2$ takes place, being these species responsible for increasing the surface mineral hydrophobicity, which enhances flotation [1, 15]. The formation of these products has been extensively confirmed by several spectroscopic techniques, such as XPS, Raman, Atomic Force Microscopy (AFM) and FTIR [10,16-18]. Although, there is a large amount of similar studies; the full understanding of the electrochemical reactions between galena and xanthate seems to be not completely understood. It is probably because differences in the galena samples being analyzed or the limitations of the techniques used in these studies. On the other hand, besides a large amount of voltammetric and optical spectroscopy studies reported in literature, there are just a few studies concerning the double-layer capacitance behavior of the system, in addition to electrochemical impedance spectroscopy studies for galena/xanthate interface [3, 19, 20]. Hui-zhong et al. investigated the galena-pyrolusite co-extraction in sodium chloride solutions by EIS [19]. Their results demonstrate that during the oxidation process, the formation of an insoluble film on galena and pyrolusite blocks the redox process and prevents the mineral to undergo a further oxidation. On the other hand, Shumman et al. [20], studied the semiconducting behavior of galena/xanthate interface by EIS measurements. From their work is concluded that xanthate is physisorbed at approximately -0.3 V, and once adsorbed it does not suppressed the oxidation of galena, but promotes a slower oxidation process.

The aim of this work is to revisit the electrochemical and interfacial aspects of galena/xanthate interface at high thiocollector concentration, using electrochemical techniques that have not been extensively used, but they offer an opportunity to obtain new insights into this particular system. Therefore, double-layer capacitance and EIS studies on galena at 0.1 M of sodium isopropyl xanthate solution, covering a wide range of polarization potentials, are presented. A detailed analysis of the EIS spectra is carried out under the equivalent circuit approach. All the results are interpreted on the basis of the xanthate adsorption and its influence on the oxidation of galena surface.

2. EXPERIMENTAL

2.1 Electrodes and solutions

A conventional three-electrode electrochemical cell was used in this study. The working electrode was prepared with native galena samples that were previously selected and mineralogically characterized with a purity of 98.7 % [21]. Samples come from the Mining Unit Charcas located in the Mexican state of San Luis Potosí, Mexico. They were cut into a cubic shape and encapsulated in epoxy resin with an exposed electrode area of 1.2 cm². A graphite rod (0.65 cm diameter) was used as counter electrode and a Saturated Calomel Electrode (SCE) was used as a reference in all experiments. The working electrode surface was renewed before each experiment by polishing it on canvas with a 5 μm alumina suspension. None activation surface process was applied to the galena mineral [22]. The working solution was an aqueous xanthate at different concentrations (0, 1, 10 and 100 mM) added as sodium isopropyl xanthate (ALKEMIN) with 0.01M KCl at pH 8 (FERMONT) included as supporting electrolyte. All solutions were prepared with deionized water with resistance of 18 MΩ (Barnstead D4641) and the reagents were used as received. A nitrogen inert atmosphere was maintained in the cell during all experiments, and the temperature was controlled at 25 °C.

2.2 Data acquisition

Cyclic voltammetry was performed with a Solartron SI 1287 potentiostat and experimental data were collected by the commercial software Coreware[®]. The voltammetric study was carried out within a potential range from -1.1V to 1.1V at 7mV/s, starting from the open circuit potential, ca. -0.1 V in the absence of xanthate and -0.35 V in its presence, toward the positive direction for all cases. Electrochemical impedance spectra were measured with either a Solartron 1260 Frequency Response Analyzer (FRA) coupled with a Solartron SI 1287 or an A/D data acquisition card model NI PCI-6251, homemade software and a potentiostat Pine Instruments AFCEBP1. The amplitude of the potential perturbation was 10 mV, the frequency range was 20 kHz-2 mHz and seven points per decade were recorded.

The double-layer capacitance measurements as a function of the polarization potential, were obtained by impedance measurements at constant 1 kHz and variable polarization potential range (-1.1V to 1.1 V) swept at 7 mV/s. All the experimental data were collected by the commercial software

Zplot[®]. For EIS measurements a stabilization time were maintained before each experiment in order to avoid current fluctuations and to ensure the system to reach steady state

3. RESULTS AND DISCUSSION

3.1 Cyclic Voltammetry

Figure 1a shows a series of cyclic voltammograms performed in absence and presence of xanthate at different concentration used as a parameter. In absence of xanthate, it is possible to observe the typical voltammogram of galena mineral in 0.01 M KCl at pH 8 [1]. In this case, two anodic processes can be observed; the first one is associated to the formation of a layer of a semipassive S^0 at 0.5 V coming from the oxidation of galena, which has been confirmed by Raman analysis (Data not shown). The second one involves the formation of lead hydroxide produced by the reaction of lead ions and hydroxyl groups from the media. On the other hand, in the presence of xanthate, a significant modification in the shape of the cyclic voltammogram is depicted. First of all, it is possible to note a soared decrease in the current measured at 1.1 V. This is presumably due to the adsorption of xanthate on the galena surface, which inhibits the further oxidation of galena. Furthermore, in the presence of xanthate, the cyclic voltammetry shows the existence of three well defined oxidation peaks, which are more clearly evidenced at the highest xanthate concentration being used (0.1M).

The O1 peak at -0.31 V, has been previously reported by Woods and others authors [1, 5, 9-10], who have studied the oxidation of galena in similar experimental conditions to the present work. According to these previous studies, the O1 peak corresponds to the oxidation and adsorption of xanthate followed by the formation of a dixanthogen molecule X_2 , as it is stated in the following reaction:



At more positive polarization potentials, the adsorbed xanthate may electrochemically react with the galena surface to form lead xanthate and dixanthogen [5]. As a matter of fact by scanning to a more anodic potentials the O2 peak appears at -0.1 V as can be seen in Fig. 1a. In agreement to Chernyshova [10] and Junqueira et al. [1], this voltammetric peak is interpreted on the basis of the following reaction:



We have also confirmed the presence of lead xanthate and dixanthogen by a Raman analysis, for a galena sample conditioned at -0.1 V and at more anodic potential (Data not shown). Under this condition, the surface becomes hydrophobic, which favors the mineral flotation [1]. Woods [5] and Junqueira et al. [1] have proposed that after lead xanthate formation and even at more positive

polarization potentials, Pb(X)_2 electrochemically reacts to produce lead hydroxide and dioxanthogen, according to the following reaction [1,5,10]:



Reaction (3) has been confirmed by Chernyshova, who performed an in situ ATR/FTIR study of the anodic processes on a galena electrode [10]. Then, O3 peak at 0.2V is associated with the formation of lead hydroxide as has been expressed in reaction (3). Lead hydroxide provides a hydrophilic character to the galena surface, limiting its flotation [1]. On the other hand, the cathodic process depicted in Fig. 1 at -0.8 V corresponds to the reduction of oxygen traces and partial reduction of galena to Pb^0 and hydrosulfide ion.

As it can be seen in Fig. 1a, there are not negligible differences in the cyclic voltammetric responses, between the highest and lowest xanthate concentrations employed. We rationalize this behavior based on the amount of xanthate adsorbed on the galena surface. High xanthate concentration promotes a strong adsorption of xanthate and a larger amount of material adsorbed on the mineral. Then, a voltammogram with three well-defined peaks can be observed. This explanation is consistent with a similar cyclic voltammetric study in xanthate solution at intermedia concentrations ranging from 10^{-5} to 10^{-3} [10]. It is worth mentioning that xanthate concentration range presented in this work is much higher than other studies, since none activation process is applied to the galena mineral which is known reduces the required concentration [21]. Nonetheless, the explanation of the concentration effect on the adsorption it is still valid in our study taking into account that we are not applying any chemical surface treatment.

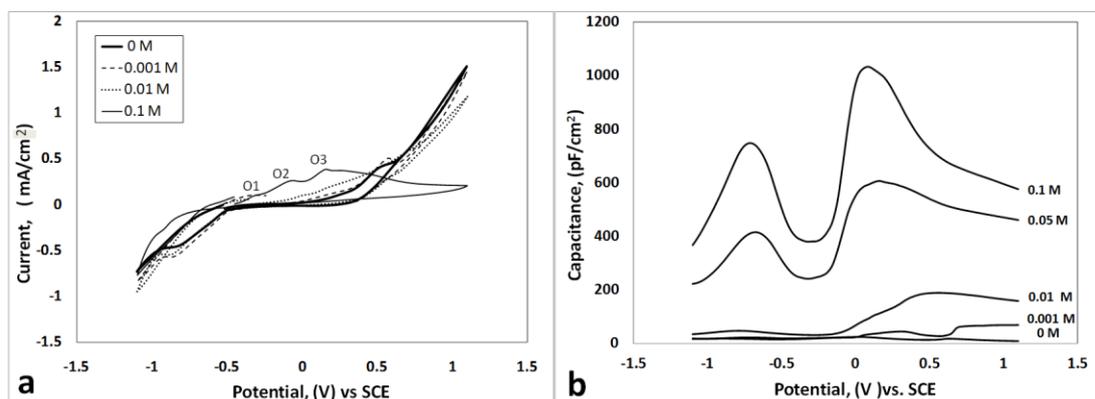


Figure 1. Cyclic Voltammograms and double-layer capacitance curves for galena immersed in KCl solution with xanthate concentration as parameter. (a) Current-potential response obtained at 7 mV s^{-1} . (b) Double-layer capacitance-potential response obtained at 1 kHz and 7 mV s^{-1} . cm^2

3.2 Double-layer capacitance measurements

The adsorption of xanthates and its relation with the electrochemical process of galena were qualitatively evaluated by double-layer capacitance measurements. Figure 1b shows the differential

capacitance-potential curves obtained with and without the presence of xanthate. As it can be observed, the double-layer capacitance values are lower in absence of the xanthate than in its presence, but systematically increase by increasing the thiocollector concentration. The difference between the shape and values of the capacitance-potential curves as a function of the xanthate concentration suggests a chemical modification of the interface promoted by a high thiocollector concentration as was already pointed out in the cyclic voltammetric results in the potential range explored. Then, at high xanthate concentration (i.e., 0.1 and 0.05 M), the double-layer capacitance curves exhibit a well defined minimum at ca. -0.3 V and a well defined capacitance pit, which ranges from -0.4 to -0.2 V. In agreement with the classical electrochemical double-layer theory [23], we have associated the minimum in the capacitance curves with the PZC. Furthermore, from the PZC it is possible to predict the potential range where xanthates adsorption is electrostatically more favorable. Thus, since xanthate is an anion, its adsorption on the galena surface is highly favorable from -0.3V and more positive potentials. On the other hand, the capacitance pit is associated with the adsorption of organic compounds [24-25] and it is the potential region where the adsorbed xanthate is stable. In a previous study carried out by Richardson and O'Dell [14], it was demonstrated that galena surface is an n-type semiconductor and it becomes sulfur deficient at a potential ca.-0.4 V, so xanthate does not adsorb onto galena at this potential. However, at more positive potentials (>-0.4 V) galena surface exhibits a p-type semiconductor properties because the polysulfide lose electrons and render to S, subsequently the surface is activated, then the adsorption of xanthates become the predominant process. In this way, our results obtained from the double-layer capacitance measurements are in fairly good agreement with similar photoelectrochemical studies previously reported [14,1]. In addition, the PZC (-0.3 V) appears at the same value than the voltammetric O1 peak observed in Figure 1a, which describes the oxidation and adsorption of xanthate and subsequently the formation of dixanthogen as it is shown in reaction (1).

At more positive polarization potentials than the capacitance pit (> -0.2 V), Figure 1b shows that the double-layer capacitance increases and the capacitance pit disappears. This behavior coincides with the modification of the galena/xanthate interface due to the electrochemical reaction (2) evidenced by O2 peak in Figure 1a. Finally, the double-layer capacitance reaches the highest value at 0.1 V, with a large modification of the interface promoted by reaction (3). It should be highlighted than these results obtained from double-layer capacitance measurements are consistent with the results found by cyclic voltammetry.

3.3 Electrochemical Impedance Spectroscopy

The adsorption-desorption xanthate process and its influence in the electrochemical oxidation of galena mineral has been evaluated by EIS in absence and presence of 0.1 M xanthate, to assure that the adsorption of the thiocollector is not negligible. The polarization potential range investigated was around the PZC. Figure 2 shows complex plane impedance spectra of galena immerse in KCl solution. From these results it is possible to observe that for all polarization potentials (-0.5 to 0.2 V), the spectra shapes are quite similar. In general, a predominant capacitive behavior is evidenced in the whole

frequency range studied. This type of impedance response can be adequately represented by an equivalent circuit which includes a constant phase element (C_{dl} , CPE) associated with the non-ideal double-layer capacitance, coupled in parallel with a resistance R_{ct} associated with a charge transfer. An additional resistance is added in series to depict the electrolyte resistance R_s .

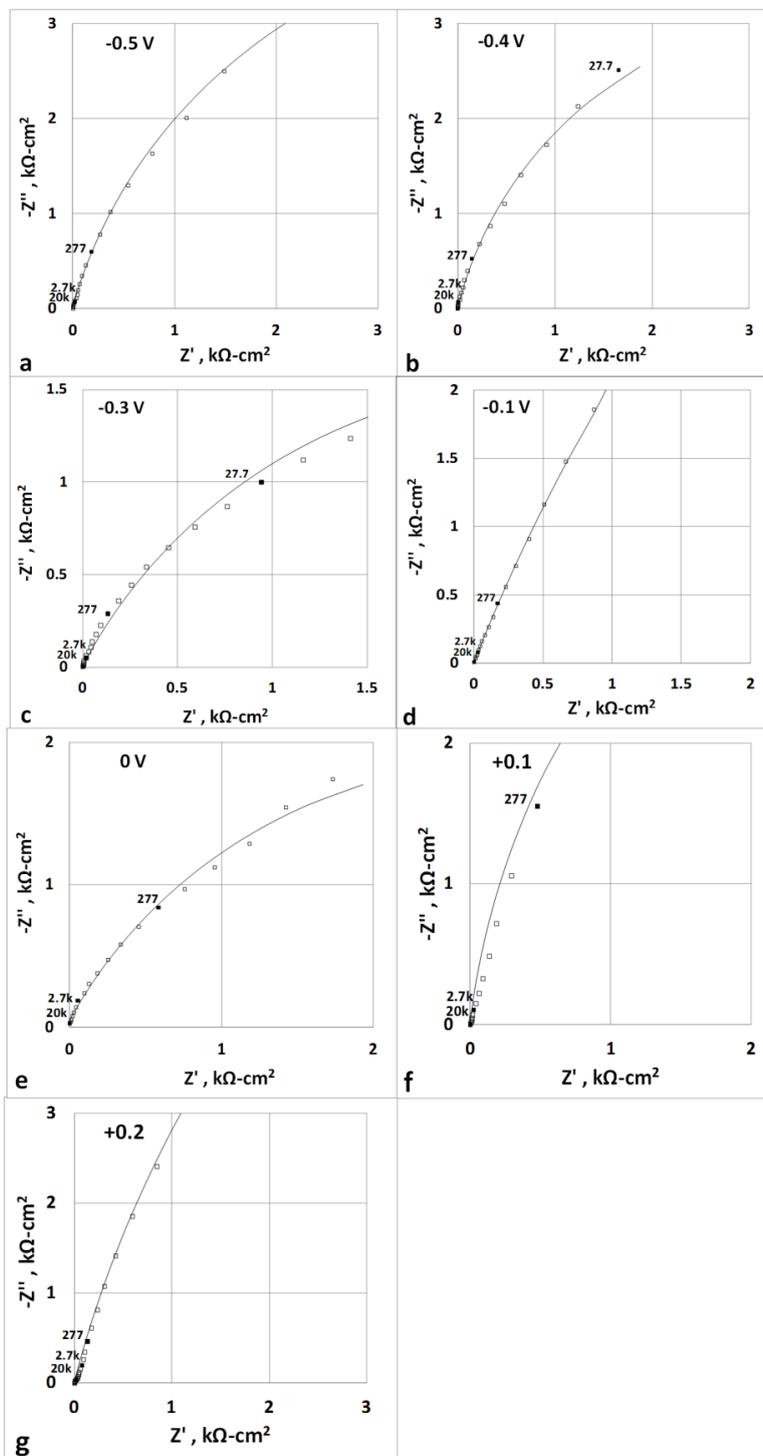


Figure 2. Complex impedance spectra for galena immersed in KCl solution at different polarization potentials. The continuous lines are the fitted spectra using the equivalent circuit shown in figure 3a. Frequency in Hertz.

This equivalent circuit (Fig. 3a) was fitted to the experimental EIS spectra by using a Levenberg-Marquardt algorithm. Table I summarizes the numerical values of each one of the electrical elements included in the equivalent circuits. The statistical fitting is adequate for all the spectra with χ^2 values around 10^{-3} .

As can be seen, the impedances are high for low frequency range reaching $1 \times 10^5 \Omega \text{cm}^{-2}$ at -0.1 V. These impedance values are attributed to an incipient charge transfer reaction associated with the sulfur activation depicted in the voltammetry analysis (Figure 1a).

On the other hand, at the highest frequency range we subtracted the solution resistance contribution to the total impedance, because they are negligible, it was done for solutions with and without xanthates.

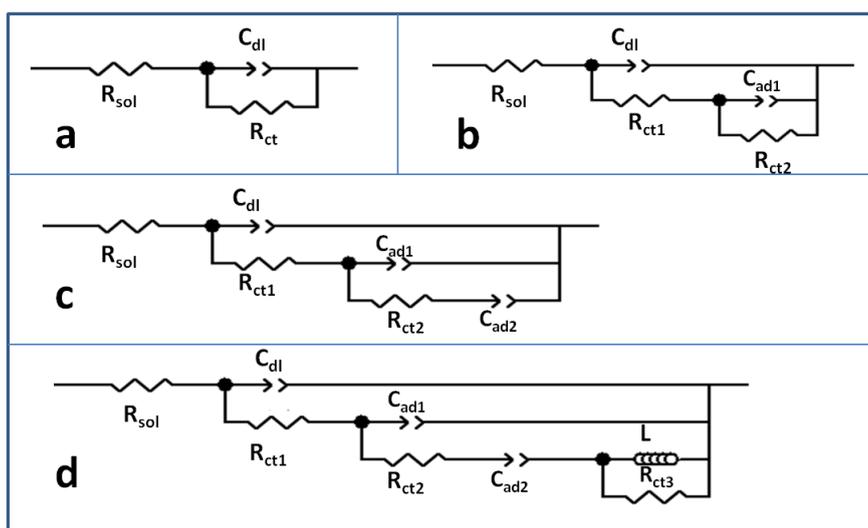


Figure 3. Equivalent circuits representing the impedance contribution of galena/electrolyte interface: (a) Equivalent circuit for galena in absence of xanthate. (b) Equivalent circuit for galena and xanthate at -0.31 V. (c) Equivalent circuit for galena in presence of xanthates at -0.1 and 0 V. (d) Equivalent circuit for galena in presence of xanthates at 0.1 and 0.2 V.

Table I. Electrical parameters obtained from the fitting of the equivalent circuit in Fig. 3a to the experimental impedance data for galena in absence of xanthate.

E (V)	C_{dl} (CPE ₁) ($\Omega \text{ cm}^{-2} \text{ s}^{-n}$)	n	R_{ct} ($\Omega \text{ cm}^2$)
-0.5	4.86×10^{-6}	0.85	9000
-0.4	3.34×10^{-6}	0.84	8096
-0.3	1.2×10^{-5}	0.77	3155
-0.1	2.04×10^{-5}	0.75	5×10^4
0	9.03×10^{-6}	0.62	3×10^4
0.1	3.14×10^{-6}	0.84	2×10^4
0.2	1.31×10^{-5}	0.87	15×10^3

Fig. 4 shows EIS spectra of galena in presence of xanthates. At negative polarization potentials (-0.5 and -0.4 V) the spectra displays a capacitive behavior, similar to the one observed in Fig 2. At the PZC (-0.310 V), two time-constant are evident in Fig. 4c and the impedance diagram obtained can be appropriately described by the equivalent circuit shown in Fig. 3b. The first time-constant τ appears in the frequency range of 20 kHz-1Hz as a depressed loop. This τ is related to the non-ideal double-layer capacitance (C_{dl} , CPE_1) coupled in parallel with the charge transfer R_{ct1} associated to the electrochemical reaction (1). It is remarked that in presence of xanthate, the charge transfer is one order of magnitude lower than in its absence (Table II). It suggests that a not negligible charge transfer is taking place at the interface as it was expected. On the other hand, the second τ which appears at a frequency below 1 Hz, is related to a second constant phase element (C_{ad1} , CPE_2) associated to a possible intermediate-adsorbed. Eventhough, this last τ looks similar to a diffusion contribution, but there is not an adequate fitting to a Warburg element. Furthermore, impedance spectra obtained subsequently did not show this behavior, it leads us to believe this second time-constant is also a capacitive loop. Under these considerations, we assume reaction (1) includes at least one intermediate-adsorbed species which remains on the electrode at this polarization potential. This assumption is in good agreement with the results founded from either double-layer capacitance measurements or previous data published by Woods [5,8]. This author proposed reaction (1) involves the adsorption of xanthate and a subsequent reaction step to form a dixanthogen molecule [1,5,10].

When the direct polarization is maintained at -0.1 V (Fig. 4d), it is possible to note that the impedance data depicts two loops as was observed in the impedance spectra at the PZC. But the equivalent circuit used to describe the impedance data at -0.1 V is different (Fig. 3c), because a careful examination of the impedance spectra at Fig. 4d, shows a more depressed loop in the range of 20 kHz to 1 Hz. In addition the real part of the impedance at 1 Hz is almost three times larger than the one obtained at the PZC. A depressed loop and its impedance values can be explained if we consider the overlapping of at least two time-constants coming from two separate processes. This assumption is supported by reactions (1) and (2) and also by the impedance spectra obtained at the PZC. Then, the loops obtained in the range of 20 kHz-1 Hz are associated to a parallel RC coupling shown in Fig. 3c. The physical meaning of C_{dl} , R_{ct1} and C_{ad1} are the same to the ones described at the PZC, while R_{ct2} represents the charge transfer involved in the electrochemical reaction (2). Additionally, at frequencies below 1 Hz, another time-constant appears in the Fig. 4d, which is related to a new constant phase element (C_{ad2} , CPE_3) which represents the $Pb(X)_2$ and S according to reaction (2), they are produced and remains onto the mineral surface. The electric parameters used in the fitting procedure are summarized in Table II. As it can be expected, R_{ct1} value decreases when the polarization potential increases due to the fact that reaction (1) is more favorable at more positive potentials. In addition the double-layer capacitance value C_{dl} also decreases suggesting that a large amount of xanthate remains adsorbed onto the mineral surface at this potential (-0.1V).

At 0 V, the experimental impedance spectrum is also adequately fitted by equivalent circuit shown in Fig. 3c, and its physical interpretation fully agrees with the explanation given for the impedance spectrum obtained at -0.1 V. However, at 0 V the presence of three time-constant are now evident, this is related to each one of the elements included in the equivalent circuit. From Table II it is possible to note that at 0 V, the double-layer capacitance C_{dl} and the charge transfer resistance R_{ct1}

associated to the first electrochemical reaction (1), decreases as was expected, but in addition C_{ad1} and C_{ad2} associated to the intermediates-adsorbed (xanthate and PbX_2, S^0) also decreases.

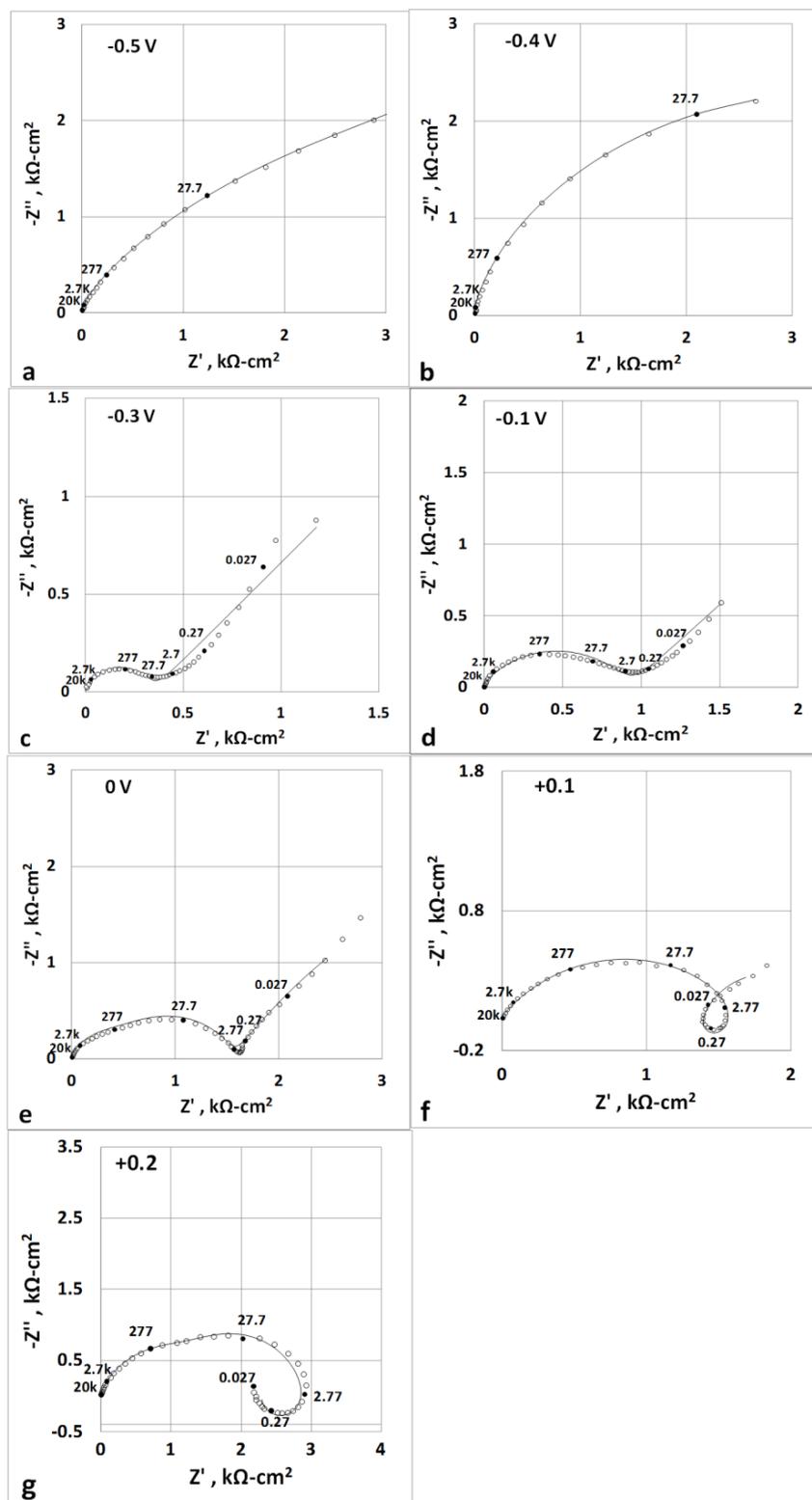


Figure 4. Complex impedance spectra for galena in presence of xanthates at different polarization potentials. The continuous lines are the fitted spectra using the equivalent circuit shown in figure 3. Frequency in Hertz.

This behavior indicate that a more compact and stable layer of intermediates-adsorbed are present onto the mineral surface, conducting to an increases of the charge transfer resistance R_{ct2} value associated to the electrochemical reaction (2). It means that the intermediates-adsorbed species are behaving as a charge transfer reaction inhibitors.

At more positive polarization potentials (0.1 and 0.2 V) Figures 4f and 4g show three time-constants, the first two τ 's at 20 kHz to 1Hz have been previously discussed.

However, at frequencies below to 1 Hz the shape of the third τ is completely different, depicting a well defined inductive loop as is observed in Figure 4f and 4g. Based on cyclic voltammetric results at high anodic polarizations it is possible to ascertain that the oxidation of the mineral and the generation of hydroxides could take place as it is established in reaction (3). Furthermore, the double-layer capacitance measurements are consistent with a chemical modification of the interface.

Table II. Electrical parameters obtained from the fitting of the equivalent circuit in Fig 3b-3d to the experimental impedance data for galena in presence of xanthate.

E (V)	C_{dl} (CPE ₁) ($\Omega \text{ cm}^{-2} \text{ s}^{-n}$)	n_1	R_{ct1} ($\Omega \text{ cm}^2$)	C_{ad1} (CPE ₂) ($\Omega \text{ cm}^{-2} \text{ s}^{-n}$)	n_2	R_{ct2} ($\Omega \text{ cm}^2$)	C_{ad2} (CPE ₃) ($\Omega \text{ cm}^{-2} \text{ s}^{-n}$)	n_3	L (H cm^2)	R_{ct3} ($\Omega \text{ cm}^2$)
-0.5	3.6×10^{-5}	0.7	4811	-	-	-	-	-	-	-
-0.4	1.01×10^{-5}	0.86	4566	-	-	-	-	-	-	-
-0.3	3.53×10^{-5}	0.71	412.3	0.00584	0.54	10000	-	-	-	-
-0.1	1.07×10^{-6}	0.94	393.2	6.98×10^{-5}	0.62	543.7	5.7×10^{-3}	0.45	-	-
0	5.21×10^{-7}	0.98	377	1.66×10^{-5}	0.73	1188	5×10^{-3}	0.58	-	-
0.1	3.1×10^{-7}	0.98	303.9	1.78×10^{-5}	0.61	1119	9.7×10^{-3}	0.50	72.6	343.1
0.2	2.14×10^{-7}	0.99	190	1.86×10^{-5}	0.48	2232	9.8×10^{-2}	0.51	136	1112

According to these results, we have correlated the existence of the inductive loop to an interface relaxation process, consisting of an interfacial rearrangement due to the adsorption-desorption of xanthate, lead xanthate, as well as the formation of lead hydroxide stated by reaction (3). Our explanations are in good agreement with similar interpretations given for inductive loops in other electrochemical systems [26-28]. Figure 3d shows the equivalent circuit fitted to the experimental impedance spectra obtained at the most positive potentials. L and R_{ct3} represent the inductive behavior and the charge transfer resistance indicated in reaction (3), respectively. Table II summarizes the numerical values of each electric element involved in this equivalent circuit (Figure 3). As it was expected R_{ct1} decreases as polarization potential increases, C_{ad1} and C_{ad2} start growing up indicating a change in the adsorption-desorption process. On the other hand, it is possible to note from Table II that at this polarization range R_{ct2} and R_{ct3} increases with the polarization potentials due to an inhibiting effect caused by the adsorbates. This last conclusion is in good agreement with the previous results founded by Hui-zhong [19], who demonstrated that an insoluble film is formed onto galena and pyrolusite and prevents them from a further oxidation.

4. CONCLUSIONS

A study of the electrochemical behavior of the galena/xanthate interface by cyclic voltammetry, double-layer capacitance measurements and EIS was presented. Cyclic voltammetric results for galena in the absence and presence of xanthate at different concentrations allows to identifying the potential at which oxidation reactions take place. At high xanthate concentration three oxidation processes are identified which include the oxidation and adsorption of xanthate, the formation of lead xanthate and subsequent formation of lead hydroxide. The influence of the adsorbates present onto the galena electrode was further studied by double-layer capacitance measurements and impedance spectra. From the double-layer capacitance curves was possible to determinate the PZC which corresponds to -0.31 V. On the other hand, the impedance spectra obtained a different polarization potentials clearly reveals the important role played by the adsorption of xanthate onto the galena surface. At the PZC the first time-constant observed at high frequencies was assigned to the oxidation of xanthate while the second one observed at low frequencies was related to the adsorption of xanthate. From -0.1 to 0 V, three time-constant were observed. The first one at the highest frequencies was associated to the oxidation and adsorption of xanthate, the second one observed at intermediate frequencies was related to the oxidation of previously adsorbed xanthate and subsequent adsorption of lead xanthate, while the third time-constant observed at the lowest frequencies was related with the presence of at intermediate-adsorbed. Finally, from 0.1 to 0.2 V an inductive process was observed at the lowest frequencies. This time-constant was associated with the relaxation of the interface due to the amount of adsorbed species and the formation of lead hydroxide.

ACKNOWLEDGEMENT

E.D. Moreno-Medrano acknowledges scholarship granted by CONACYT. Also, authors acknowledge to Francisco Galindo and Erasmo Mata from UASLP for the electrodes preparation.

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