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# Redox behavior of galena in alkaline condition

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**Abstract** Electrochemical potential determines types of redox products formed on electrically conducting minerals like galena, which might manipulate process efficiency applied on the target mineral. Therefore, electrochemical behavior of galena has utmost importance for flotation and hydrometallurgical applications. This study was performed to elucidate redox behavior of galena by cyclic voltammetry (CV) technique in a wide potential range. Voltammograms were obtained at pH 9.2 using deoxygenated borate buffer solution in a three-electrode system electrochemical cell. CV tests revealed that redox reactions proceeded reasonably irreversibly on galena electrode. Pb-oxyhydroxides released on the electrode together with sulfoxy species during anodic process while oxygen containing Pb-species reduced to metallic lead at highly reducing potentials. Oxidation product was thought to form a porous layer on mineral surface. Anodic oxidation process of galena obeyed hypothetical polarization diagram. Beyond transpassive surface corrosion, further oxidation of galena proceeded at highly oxidizing potentials at a limit current due to formation of porous Pb-oxide + sulfoxy layer.

**Keywords** Galena · Cyclic voltammetry · Polarization · Redox reaction

## Introduction

Galena (PbS) is a semiconducting sulfide mineral, and is the main source of lead metal. Similar to other semiconducting

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sulfide minerals, galena oxidizes in pulp medium releasing metal ions and hydrophobic S° on the mineral surface (reaction 1). Formation of S°-rich, metal-deficient zones promote the natural floatability of sulfide minerals especially in mildly acid environment [1–3]. The hydrophobic surface species appear as metastable phases at alkaline pHs, and then oxidize further during extended conditioning. Excess surface oxidation produces hydrophilic sulfoxy species together with the re-adsorption of metal ions on mineral surface as hydrophilic hydrolysis products [2–6]. Oxidation states of sulfide minerals differ from each other depending on the nobility of dissolved metal ions and mixed potential of flotation pulp at given pH [2, 4–9]. Therefore, floatability of sulfide minerals varies with the applied potential and stability potential range of redox products of different sulfide minerals. Previous works revealed that galena could selectively be floated by sulfhydryl type collecting agents around pH 9 [1, 10, 11]. Pulp potential decreases at higher pHs, and galena flotation deceases even in the presence of collecting agent due to heavy coatings of mineral surface by hydrophilic lead species [1, 2, 10–12].

$$PbS \leftrightarrow Pb^{+2} + S^o + 2e^- \qquad (1)$$

Pulp potential is also important in hydrometallurgical applications. Leaching is an electrochemical process in nature. Leaching in acid environment is preferred due to high solubility of metal ions. However, several problems have been encountered like contamination of acid leached Pb-liquor with other metals, high acid consumption, and necessity for complex purification processes [13, 14]. Then, alkaline leaching has been investigated as an alternative method despite some disadvantages like low solubility and slow reaction rate in NaOH leaching medium [15–17]. Alkaline leaching has allowed the recovery of Pb-leach liquor with higher selectivity as compared with acid leaching. Some contaminating metals

remain in the solid residue in alkaline leaching indicating necessity of simpler metal extraction process from leach liquor [16, 18, 19]. Badanoiu et al. [15] proposed that lead could be recovered in NaOH leaching circuit in the form of sodium plumbite, which is further processed in electrolysis cell to deposit the reduced Pb-metal on cathode.

Great interest has focused on the redox behavior of galena in relation to flotation and hydrometallurgical processes. It oxidizes irreversibly around open circuit potential [4]. PbO and S° were found to form on galena surface by cyclic voltammetry (CV) tests as a result of alteration by anodic processes [1, 5, 13, 20]. Anodically oxidized species has been proposed to reduce in cathodic process releasing Pb° on the mineral surface at reducing potentials instead of PbS formation as a reversible process [13, 21]. Based on linear sweep voltammetry experiments [5], irreversibility of redox processes was attributed to the further oxidation of galena beyond PbO and S° to the formation of Pb-oxyhydroxy species and irreversible oxysulfur anions. Urbano et al. [7] discussed the effect of anodic oxidation limit on the type and amount of oxidized and reduced products of galena in neutral condition. Jin et al. [22] explained electrochemical dissolution of galena by acidity/alkalinity. They proposed that charge transfer resistance in the double layer decreased in the presence of large quantity of $H^+$ or $OH^-$ ions. Nava et al. [23] studied the anodic dissolution of galena by CV method in perchlorate medium, and proposed that its anodic dissolution was inhibited by the formation of elemental sulfur on the mineral in mild to moderately oxidizing conditions. They also pointed out that electro-dissolution of galena was only partially inhibited at highly oxidizing potentials due to oxidation of S° to porous thiosulfate and lead sulfate species. Aghassi et al. [24] investigated the electrochemistry of PbS semiconducting film deposited on stainless steel in neutral condition by voltammetry tests. Oxidative dissolution was found to occur in mild to moderately oxidizing condition. They concluded that electrode surface was not passivated by sulfate species.

Electrochemical behavior of galena has utmost importance both for flotation and hydrometallurgical applications. Galena flotation is a potential dependent process. Redox products might improve natural hydrophobicity/floatability or promote the adsorption of thiol collecting agent, or vice versa. Hence, detailed investigation on electrochemical behavior of galena in a wide potential was thought to be beneficial. Similarly, galena leaching, and then recovery of metallic Pb from leach liquor are electron transfer-based processes. Success of galena leaching necessitates the clarification of its redox behavior in the whole potential range where hydrometallurgical processes can be applied. This work was performed to contribute to the understanding of the redox behavior of galena in a wide potential range. The characterization of galena oxidation was studied by physical electrochemistry methods. Test works were conducted in alkaline condition to make electrochemical dissolution of galena more apparent [22].

## Materials and methods

Study was made using highly mineralized galena specimen. Sample was supplied from galena-sphalerite ore deposit in Sivas, Turkey. Mineralogical constituent of crystal sample was determined by XRD analysis while SEM-EDS measurements were applied to identify chemical composition. Crystal samples were found to be highly pure, and sphalerite was the sole trace impurity.

Tetraborate (0.05 M $Na_2B_4O_7x10H_2O$) solution was prepared to obtain pH 9.2 buffer, and used in electrochemical works. Experiments were performed in oxygen-free environment to eliminate the oxidizing effect of dissolved oxygen in the buffer solution. For this aim, intensive purging of highly pure nitrogen gas (99.998% $N_2$) was applied. Oxygen content of buffer solution was measured by YSI-5100 oximeter.

Three-electrode system electrochemical cell and a potentiostat were used in electrochemical works. CV tests were performed in stagnant buffer solution by Gamry PCI-750 potentiostat at room temperature. Galena crystal was employed as working electrode while reference electrode was Ag-AgCl electrode. Mineral crystal was cut, and mounted into a glass tube with an electrochemically inert epoxy. Electrical connection of working electrode to potentiostat was satisfied using Cu-wire and Hg. Pt-foil was used as counter electrode. Voltammograms were drawn by using PHE-200 Physical Electrochemistry software of Gamry Co. manipulating the potential range and scan rate. All the measured potentials were converted from Ag/AgCl reference electrode scale to standard hydrogen electrode (SHE) scale by adding 200 mV to the measured values.

Fresh working electrode surface was obtained rubbing the exposed area of electrode with 1000 grit Si-C emery paper, and polishing with 1 μm diamond paste prior to each test. Then, electrode was rinsed intensively with distilled water, and immediately transferred into the deoxygenated buffer solution. At least six cycling was applied in each CV test to eliminate possible oxidation due to exposure of electrode surface to atmospheric oxygen during surface cleaning stage. Scanning was applied in cathodic direction starting from the upper cycling limit to avoid the possible misunderstanding arising from redox behavior of possible surface oxidation products coming from electrode preparation stage.

## Results and discussions

Cyclic voltammogram of galena was drawn in a wide potential range (−1000 + 1000 mV) as shown in Fig. 1a. Scanning was started from upper potential limit in cathodic direction. Four peaks were obtained in anodic region while two reduction peaks formed in cathodic scan. Additionally, a new cathodic peak (C3) started to appear towards lower scanning potential limit.

Galena was thought to oxidize (reaction 2) during electrode preparation stage just before CV test due to high reactivity of exposed mineral surface in spite of great care given to minimize oxidizing effect of atmospheric oxygen [1, 13, 22, 24]. Metal-hydroxides might also form by anodic decomposition of galena surface (reaction 3) together with the formation of oxysulfur species, such as metal-thiosulfates and sulfates [7]. The redox products of electrode preparation stage were reduced by scanning the electrode surface in cathodic direction. Small shoulder around −550 mV (C1) and sharp peak (C2) at about −680 mV were obtained in the first cathodic cycle on the voltammogram (Fig. 1a). Current of redox peaks increased by repetitive cycling except C1, and came to closer to equilibrium at the last cycle (Fig. 2). On the other hand, that of C1 decreased in first three cycles, and then increased gradually in the following ones forming an inverse shoulder. Released elemental sulfur reacts with PbO in cathodic scan to form PbS again proceeding the reaction 2 in reverse direction forming C1 [13]. Peak C1 gradually disappeared up to third cycle due to restricted release of S° in fresh electrode surface preparation stage, and/or reasonable tendency of S° to oxidize irreversibly

to form porous sulfur-oxy species at higher potentials [5, 6, 23]. Negligible amount of S° contributes to the reduction process, and infinitesimal amount of oxidized species will reduce to original form (reactions 2, 3).

$$PbS + H_2O \leftrightarrow PbO + S^o + 2H^+ + 2e^- \tag{2}$$

$$PbS + 2H_2O \leftrightarrow Pb(OH)_2 + S^o + 2H^+ + 2e^- \tag{3}$$
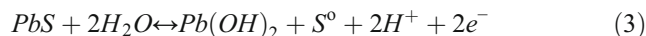
Relationship between anodic and cathodic peaks was investigated by changing the switching potential both from upper (Fig. 1b-d) and lower (Fig. 1e-g) limits. Switching points were determined as the appearance potential of main redox peaks. Intensities of peaks were almost at negligible current levels in narrowed scan ranges as compared with that of full range. Some peaks disappeared when scan range was reduced both from anodic and cathodic reverse limits. When anodic scan was reversed from −500 mV, only peak C3 formed (Fig. 1d). Galena is thermodynamically not stable at highly reducing condition, and then reduces to metallic form according to reaction 4 [24]. When cathodic scanning was reversed and continued in the anodic region, an oxidation peak formed weakly at about −625 mV. Anodic dissolution of metallic lead occurred in the reverse scan according to reaction 5 [7, 20]. $Pb^{+2}$ ions on the interface satisfy greater porosity of the new surface film on the electrode [23, 25]. However, intensity of C3 decreased at repeated cycling due to decreased oxidation rate of Pb° to ionic form. Size of peak C3 was observed to be lower than anodic
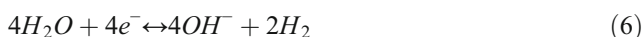


**Fig. 1** Galena voltammograms drawn in different scan ranges
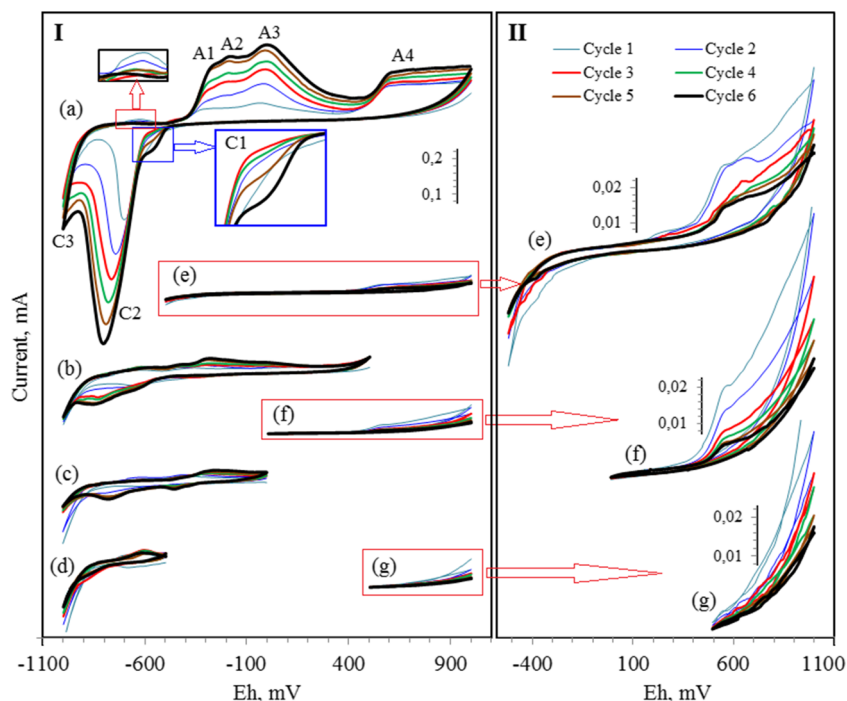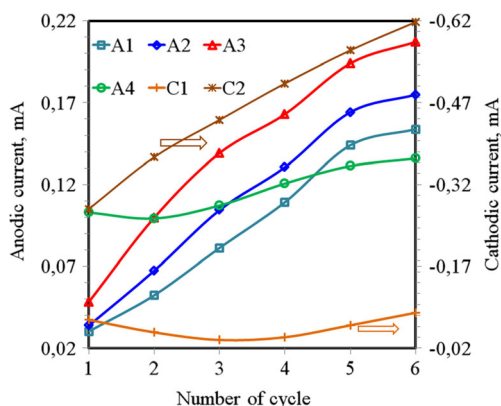
**Fig. 2** Effect of cycling on the current of redox peaks

shoulder. This difference arose from cathodic decomposition of water (reaction 6).
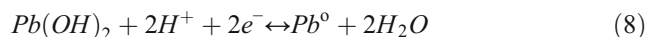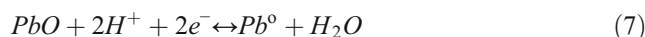
$$PbS + H_2O + 2e^- \leftrightarrow Pb^o + HS^- + OH^- \qquad (4)$$

$$Pb^o \leftrightarrow Pb^{+2} + 2e^- \qquad (5)$$

$$4H_2O + 4e^- \leftrightarrow 4OH^- + 2H_2 \qquad (6)$$

Oxidation peak at about −625 mV was also seen in full scan range (Fig. 1a). It shaped as a hardly detectable peak, and almost disappeared after 3rd cycle. $Pb^{+2}$ ions could only present in metastable phase at oxidizing potentials [5, 13]. Then, metallic form was thought to oxidize directly to stable Pb-oxides (peaks A1, A2 and A3) by several oxidation reactions including metastable phases [8, 26].

Peak C2 and peak group-A1, A2, A3- appeared when extending the anodic switching limit up to 0 mV (Fig. 1c). But, anodic peaks were so weak that they could not individually be defined. Those peaks could even not be discriminated in the extended anodic scan range to 500 mV (Fig. 1b). Redox products covered electrode surface irreversibly in narrower scan ranges so that applied potential was not enough to overcome the resistance of passive layer for further oxidation. Full effect could only be observed by switching the anodic scan from 1000 mV, where resistance of passive surface coating was overcome, and further oxidation occurred at a certain rate (peak A4).

Irreversible surface oxidation species confined the reduction (peak C3) of unoxidized PbS sites. These species reduced to metallic form shaping peak C2 in cathodic scan according to reactions 7, 8 and the like. Size of C2 was doubled shifting the anodic reverse limit from 0 mV to 500 mV (Fig. 1b-c). But, similar increase in the current of the peak group-A1, A2, A3- was not observed. Broad shape of peak C2 in Fig. 1b might be explained with the appearance of peak A4 releasing PbO. Elemental sulfur would also form during galena oxidation together with sulfur-oxy species. They reduced mainly to $HS^-$ in cathodic scan contributing to the size of C2. Moreover,

reduction of unoxidized galena surface according to reaction 3 was another source of $HS^-$ release. In anodic scan, HS- was thought to oxidize to form elemental sulfur-S° according to reaction 9 [8, 9]. This anodic process is expected to appear around −200 mV, which is in the range of peak group-A1, A2, A3.

$$PbO + 2H^+ + 2e^- \leftrightarrow Pb^o + H_2O \qquad (7)$$

$$Pb(OH)_2 + 2H^+ + 2e^- \leftrightarrow Pb^o + 2H_2O \qquad (8)$$

$$HS^- \leftrightarrow S^o + 2H^+ + 2e^- \qquad (9)$$

Passive behavior of surface oxide film was clarified by manipulating the cathodic switching potential. When reversing the switching potential from 500 mV (Fig. 1g), anodic current increased continuously but peak A4 could not be clearly discriminated. It became apparent in the scan range 0–1000 mV (Fig. 1f). Any reduction peak was not observed in this range indicating irreversible formation of oxide layer on the electrode surface [23]. Current of A4 decreased sharply first during repetitive cycling, and then gradually, drawing a parabolic curve (Fig. 3). This oxide layer displayed reasonably porous property. It reduced current flow at repeated cycling, but not completely inhibited the electron flow. At repeated cycling, thickness of porous layer was thought to increase causing increased resistance to electron flow and diffusion of redox components into the reaction sites [27, 28]. Whenever cathodic scan was switched from −500 mV (Fig. 1e), certain amount of anodic products was reduced to PbS forming peak C1 [5, 13]. In this case, electron transfer rate constituting peak A4 did also increase slightly possibly due to relatively reversible oxidation of galena to PbO. Increase in current became sharper especially above 700 mV. This potential is around the upper stability
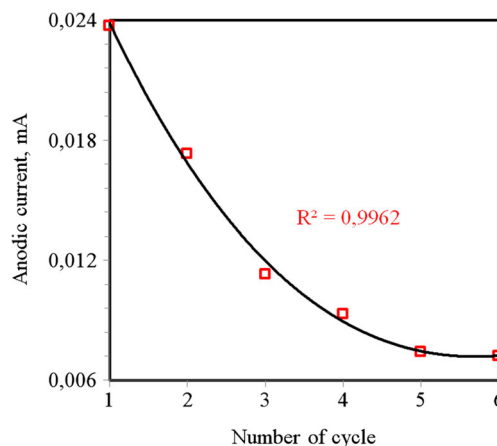


**Fig. 3** Change in the anodic current of peak A4 with repeated cycling in the scan range 0–1000 mV
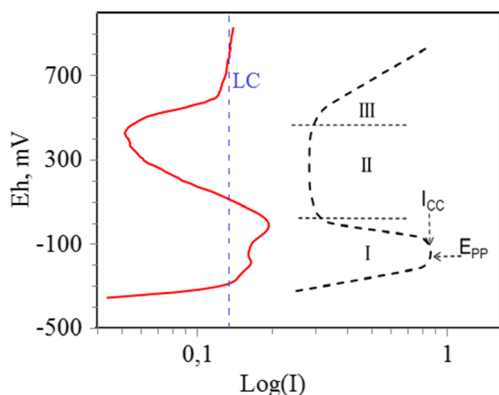
limit of water [8, 9]. $H_2O$ tends to decompose at highly oxidizing potential releasing oxygen (reaction 10).

$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \qquad (10)$$

Electrochemical processes proceeding at moderate to highly oxidizing potentials (A4) could not exceed certain limit of electron transfer rate in full scan range (Fig. 1a). The oxidation processes continued up to anodic switching potential almost at a constant current level indicating the presence of limit current (LC). The new surface film did not exhibit completely passive behavior, which only restricted the electron transfer at LC value. Elemental sulfur, the other constituent of oxidation process, did also contribute to confine current flow [23]. S° is not stable at the cited potential values, and then oxidation would continue irreversibly with the formation of porous thiosulfate and sulfates [2, 5, 6, 29].

Electrically conducting materials draw anodic polarization diagrams (PD) in certain potential range in electrochemically active aqueous environment (Fig. 4). Hypothetically, these diagrams contain three different regions: I- active region, II- passive region, III-transpassive region. During anodic polarization, current increases in active region sharply with a step-by-step change in potential. Current flow increased, and reached up to a critical value ($I_{CC}$) at passivation potential ($E_{PP}$), and then decreases down to equilibrium level, where passive region starts. Electrochemical activity of tested materials will be at minimal level in the passive region. Electron flow does not completely decease down to zero. Rate of electron flow in this region depends on the resistance of passive layer. When potential just reaches to upper stability limit of passive surface layer, anodic oxidation starts again to proceed especially on weak sites of passive layer, where is named as transpassive region [4, 30].

Anodic polarization diagram of galena does almost fit to the hypothetical one (Fig. 4). Active region drew a bit larger curve due to continuous oxidation of several reduced species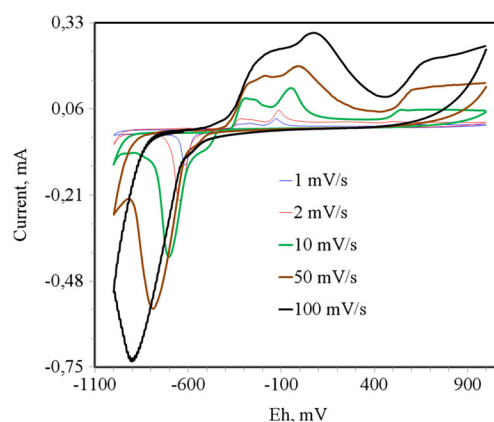 forming peaks A1, A2 and A3. Current did not decrease sharply towards the end of active region. Oxidation processes continued at decreasing order up to about 400 mV possibly due to resistance of new surface film against electron flow. Passive region was observed to be reasonably narrow. Surface oxidation, then, continued in transpassive region. Further oxidation in transpassive region produced a porous oxide layer–porous film of PbO + Pb-sulfoxy species [31, 32]. This layer behaved like a screen surface and confined electron flow at a certain current value (LC). Actually, starting potential of LC may be viewed as the appearance of a new passive layer.
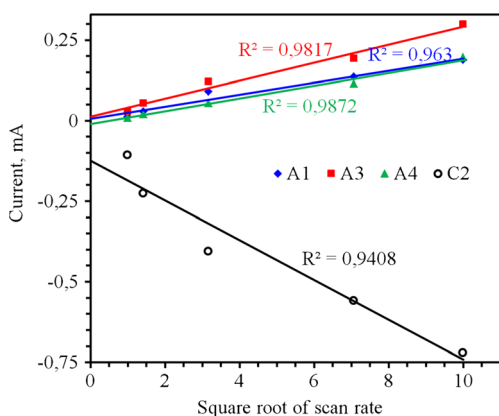
Peaks A1, A2 and A3 did not form when switching the scan from narrowed cathodic limits (Fig. 1e-g). They were observed only when cathodic limit was stretched down to −1000 mV. Therefore, manipulation of cathodic scan limit did also prove that anodic maxima -A1, A2, and A3 should be in relation with peak C2. Reduction peak C2 formed sharply even in the first cycle in full scan range. This peak was attributed to the formation of metallic lead according to reactions 6, 7 in addition to reduction of S-bearing species to $HS^-$ [2, 4, 5, 21].

Kinetics and reversibility of redox reactions can be identified by giving them enough time to proceed. CV study is an excellent way of clarifying the redox behavior of a conducting material in terms of size and formation potentials of maxima at different scan rates on the voltammograms. Lower scan rate, which means higher polarization time, might be necessary in some cases for certain electrochemical processes, or kinetics of electrochemical processes might be fast enough to apply higher sweep rates in some other cases [33, 34].

Voltammetric behavior of galena was examined at various scan rates (Fig. 5): no new peak was obtained, and peak structure did not change besides expected increase in peak size at higher scan rates. But, peak separation between anodic and cathodic peaks increased. Maximum current points of anodic peaks shifted to oxidizing values whereas that of C2 shifted in inverse direction without deviation in the starting potentials of redox peaks. Larger peak separation at higher scan rates was associated with slow electron transfer and/or change in the



**Fig. 4** Anodic polarization diagram of galena (Dashed curve: hypothetical anodic polarization diagram; LC: limit current)



**Fig. 5** Cyclic voltammograms of galena at different scan rates

**Fig. 6** Relationship between peak current and scan rate

composition of the passive layer [33, 34]. Redox behavior of galena was thought to be mainly controlled by the degree of the passive behavior of PbO, an oxidation product coming from dissociation of fresh galena surface (peak A4). Potential of peak maximum of A4 was almost not affected from polarization time, which proved the porous structure of surface oxide layer.

Relationship between peak current and scan rate is defined by Randle-Sevcik equation given below, where $i_p$ is the peak current (ampere), n is electron stoichiometry, A is the electrode area ($cm^2$), $c°$ is the concentration ($mol/cm^3$), D is the diffusion coefficient ($cm^2/s$), and v is the scan rate (V/s). There will be a linear relationship between square-root of scan rate and peak current for a reversible process providing no deviation in formation potential. Fig. 6 shows the change in peak current of galena electrode with respect to square root of scan rate. Anodic peaks drew almost liner relationship passing through the origin. But a reasonable deviation from the origin occurred in case of C2, which behavior was attributed to diffusion-controlled processes [6, 34]. Peak C2 was referred to the reduction of Pb-oxides to metallic form in addition formation of $HS^-$. Lower $R^2$ value and significant deviation of the curve of peak C2 from linearity were thought to be sign of lower reaction kinetics of reduction processes shaping C2, and therefore lower reversibility rate of reduction processes.

$$i_p = 2.69x10^5 n^{3/2} Ac°D^{1/2} v^{1/2} \qquad (11)$$

## Conclusions

Voltammetric behavior of galena was investigated in a wide potential range ($-1000 + 1000$ mV) at pH 9.2. Following conclusions were drawn from experimental works:

– Galena oxidation was a reasonably irreversible process. Surface oxidation products were thought to be Pb-oxyhydroxides and sulfoxy species. Pb-species reduced during cathodic process to metallic form at highly reducing condition.

– Redox products formed a porous layer on galena, which did not completely inhibit redox processes both in anodic and cathodic scan.

– Anodic oxidation process of galena obeyed hypothetical polarization diagram. In active region, Pb oxidized to PbO together with the formation of S°, which caused surface passivation in a limited potential range. Galena started to oxidize again above 400 mV in transpassive region forming porous Pb-oxide + sulfoxy layer. Beyond transpassive surface corrosion, further oxidation of galena proceeded at highly oxidizing potentials at a limit current due to presence of this porous layer.

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