

# CYCLIC VOLTAMMETRIC STUDIES ON SPHALERITE ELECTRODES

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**Cyclic voltammetric studies on sphalerite compact electrodes containing 30% Graphite and 10% pitch and carbon paste electrodes have been carried out in sulphuric acid of concentration 0.5N, 1.0N and 2.0N at different scan rates. The open circuit voltage varies from 200 to 300 mV. It has been observed that the dissolution current increases with acid concentration and scan rate. The peak current also increases slightly if the initial potential is changed from 0 to -0.4 V. The cyclic voltammogram shows the oxidation of ZnS, the product, sulphur in the forward cycle and the reduction of the oxidation product in the reverse (cathodic) cycle. The peak potential shifts anodically, as the scan rate is increased; but shifts to less anodic potential with the rise in the concentration of the acid.**

**Keywords:** Sphalerite, cyclic voltammogram, anodic polarisation, electroleaching, anodic dissolution

## INTRODUCTION

Zinc is an important metal, which finds extensive application in various fields including agriculture and rubber making. The demand for the metal is day by day increasing. Zinc occurs in nature as sulphide ore and is produced both by pyrometallurgical and electrohydrometallurgical processes. Direct recovery of the metal from zinc concentrate were attempted as in the case other base metal sulphides [1]. The present investigation was undertaken to study the electrochemical oxidation of sphalerite using cyclic voltammetric technique.

## EXPERIMENTAL

In the direct electrolysis of sulphides the major problem is the fabrication of a stable electrode. In the case other base metal sulphide the electrodes can either be massive mineral itself or cast type. But in the case of sphalerite it can not be casted and the electrodes are fabricated using compaction technique. As sphalerite in pure form is regarded as an insulator with a resistivity of 10-10 ohm cm [2,3], it has to be mixed with a conducting inert material like graphite. The composition of sphalerite concentrate used in this investigation is given in Table I

For the present study sphalerite concentrate is mixed with 30% natural beneficiated graphite and 10% pitch and the mixture is compacted in a die at a pressure of 46.4 KN cm<sup>-2</sup> and heat treated at 423K. The detailed preparation has been described elsewhere [4]. The electrical connection to the pellet is effected through a platinum wire embedded during compaction process. A thin insulated Copper wire is soldered

to the platinum wire. The exposed wire portion and one face of the electrode are masked with an epoxy resin. These compacts possess sufficient strength with a resistivity less than 2 ohm cm. Electrodes used for the study have an area of 0.7854 cm<sup>2</sup>.

For the cyclic voltammetric studies a Potentiostat (Wenking model POS73) which is a Combined version of Potentiostat and Scan generator is used. The study comprises anodic sweep followed by a cathodic sweep between two potentials. The current output is recorded as a function of input potential using a Rikadenki X-Y recorder model Rw 2017. Each time the electrodes are polished with emery sheets, 1/0 to 4/0 and washed well with distilled water. Cyclic voltammograms are taken only after the electrodes are allowed to attain the equilibrium potential. All potentials referred to in the text are with reference to saturated calomel electrode.

## RESULTS AND DISCUSSION

Cyclic voltammetric studies on sphalerite compacts have been carried out in sulphuric acid of concentrations 0.5 N.

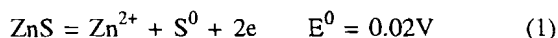
**TABLE I: Partial chemical composition of sphalerite**

Element	Percentage
Zn	50.50
S	31.61
Fe	8.08
SiO <sub>2</sub>	4.06
Pb	1.74
Cd	0.81

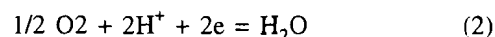
1.0 N and 2.0 N at different scan rates. The open circuit potential varies from 200-300 mV. A typical cyclic voltammogram of sphalerite compact in 1.0 N  $\text{H}_2\text{SO}_4$  at potentials ranging from 0 to 1.5 V at  $20 \text{ mVs}^{-1}$  is given in Fig.1. It is seen that the current increases rapidly, with increase in potential forming a well-defined peak 'A1' at 560 mV and then decreases till a potential of 800 mV is reached. Thereafter again it increases continuously till the final potential is reached. A small broad kink 'A2' is observed at a potential of 1.1V. On reversing the sweep at 1.5 V the current drops slowly and is anodic upto a potential of 600 mV indicating the dissolution of sphalerite and thereafter the current decreases rapidly. A peak 'C' is observed at 180 mV, which is not sharp. Considering the potentials at which peaks are observed the following electrochemical reactions are envisaged.

#### Peak A1

The main reaction at this peak is the oxidation of  $\text{ZnS}$ , as shown by the equation given below:



Price and Warren [5] have also obtained similar results when  $\text{ZnS}$  is anodically polarized in 1N  $\text{H}_2\text{SO}_4$  (maximum current at 0.61 V) Kunieda et al. [6] and Oki et al. [7] have suggested that graphite or a noble metal sulphide can act as galvanic couple and oxygen reduction takes place at the cathode by the following reaction:

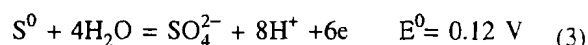


Hence it is expected that oxygen has a significant effect on the rate of dissolution. But Narasagoudar et al. [8] observed no change in the rate of dissolution when either oxygen or nitrogen sparging is used. This suggests that during polarization, most of the  $\text{Zn}^{++}$  is produced electrochemically.

#### Peak A2

This peak can be attributed to the oxidation of the product formed during the anodic dissolution of  $\text{ZnS}$ .

The product, S, is thermodynamically oxidisable at much lower potential. Since there is no oxidation of sulphur upto a potential of 800 mV, the oxidation may occur with overpotential [9] at this value. The reaction, which occurs, can be described by the following reaction:



A similar behavior has also been observed by Choi et al. [10]. Another evidence which may be got for the formation of sulphate is that when electrode is held at 1.5 V for sometimes (10 secs), the current during the reverse sweep is much more anodic than the one when the sweep is reversed immediately after reaching 1.5V.

This is described in Fig.2. The possible reason may be that during the anodic sweep all the sulphur formed on the electrode surface might not have been oxidized within the short span of time. Hence the current starts decreasing

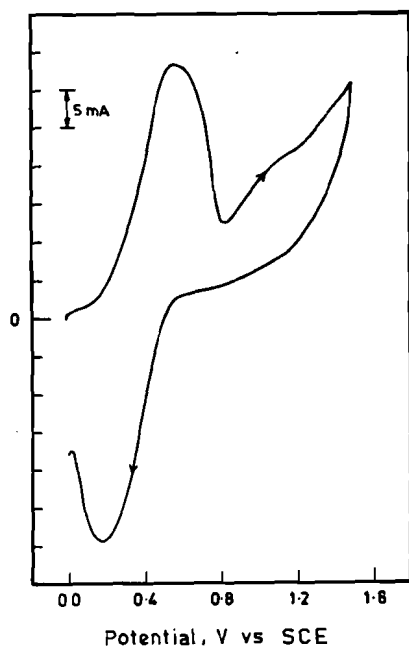


Fig.1: Cyclic voltammogram of sphalerite compact electrode in 1 N  $\text{H}_2\text{SO}_4$ . Sweep rate  $20 \text{ mVs}^{-1}$

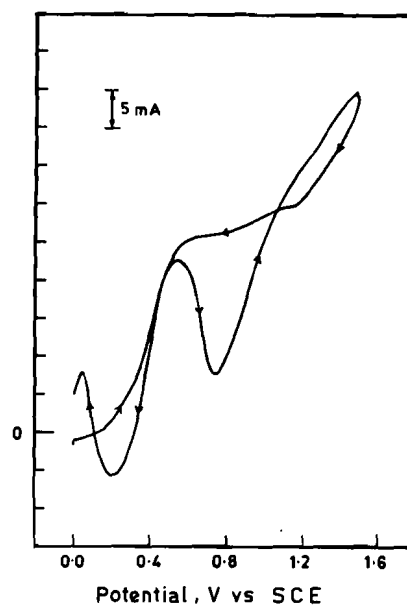
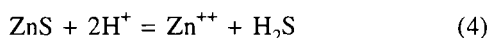
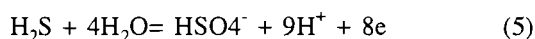


Fig.2: Cyclic voltammogram of sphalerite compact electrode in 1N  $\text{H}_2\text{SO}_4$  held at 1.5 V for 10 seconds. Sweep rate  $20 \text{ mVs}^{-1}$

immediately after the reversal of the sweep due to the blockage by sulphur on the surface of the electrode. Once the sulphur is oxidised to soluble sulphate by the prolonged polarisation of the electrode at 1.5V the surface area of the electrode exposed is much larger than the previous case and hence the increase in the anodic current in the reverse sweep. It has been observed by Narasagoudar et al. [8] that when ZnS is potentiostatically polarised at 0.61 V, the  $\text{Zn}^{++}/\text{S}$  ratio was found to be greater than one suggesting either sulfur removal by the reaction (3) or by the production of excess  $\text{Zn}^{++}$  ion by the following reaction:



The  $\text{H}_2\text{S}$ , which is unstable at this potential, may be oxidized by the reaction (5)

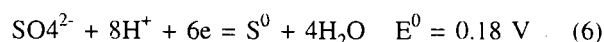


But when the electrode is polarized at 0.26 V, the  $\text{Zn}^{++}/\text{S}$  ratio was found to be 1.04 [1] suggesting the absence of sulphur oxidation or the formation of  $\text{Zn}^{++}$  through equation (4). Hence in all probability above 0.8V the main reaction that removes sulphur is its oxidation to sulphate, which is in

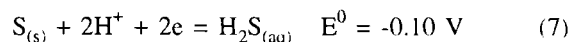
confirmity with the observed result. Other researchers [11,12] have also noticed similar behaviour.

### Peak C

During reverse scan a cathodic peak is formed at 0.18V. This may be the reverse reaction of equation (3), which may be represented as:



or by the reduction of S



If the reaction mentioned in equation (6) is the only reaction, the electrode surface is expected to be covered either fully or partially by sulphur and the area of the electrode exposed in the subsequent cycle is expected to be less. Even in the case of chemical oxidative dissolution of zinc sulphide and other metal sulphides the sulphur formed on the mineral particle surface controls further dissolution. Hence the peak current should be less than that in the 1st cycle. In actual practice it can be seen from Fig.3 that the current increases

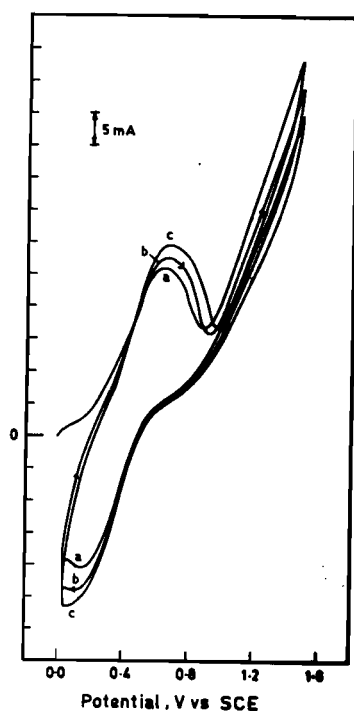


Fig.3: Effect of cycling on the voltammogram of sphalerite compact electrode in 1 N  $\text{H}_2\text{SO}_4$ . Sweep rate  $20 \text{ mVs}^{-1}$  (a) 1st cycle (b) 2nd cycle (c) 3rd cycle

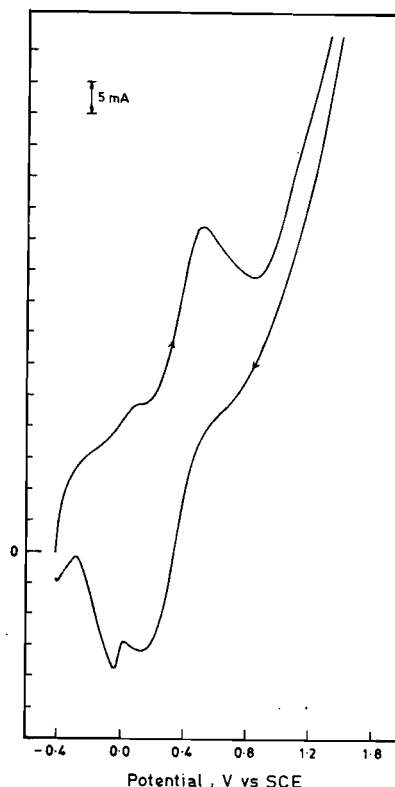
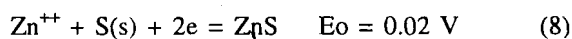


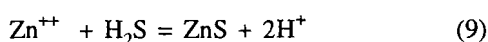
Fig.4: Cyclic voltammogram of sphalerite compact electrode in 2 N  $\text{H}_2\text{SO}_4$ . Sweep rate  $5 \text{ mVs}^{-1}$

in subsequent cycles and hence it can be assumed that after this reaction, the sulphur thus produced also undergoes a reduction process and gets reduced to  $H_2S$ . This reaction may result in the removal of blocked surface, though the product  $H_2S$  may also adsorb on the surface. This action should end up either with the maintenance of same level of anodic peak current or increased amount of current due to the increase in porosity of the compact as some  $ZnS$  molecules have already reacted.

The other possibility is the reduction of  $Zn^{++}$  to  $ZnS$  i.e. the reverse of the reaction mentioned in equation (1), which can be written as follows:



$ZnS$  formed in this way may be expected to be an insulator, as this film does not make a good contact with the graphite. This has been proved [8] by passing  $H_2S$  through the solution, which precipitates  $Zn^{++}$  as  $ZnS$  on the electrode, by the reaction.



and the anodic current is found to be less in the subsequent cycle. Since there is no reduction in the anodic peak current in the next cycle, it may be assumed that the peak 'C' is not due to the reaction mentioned in equation (8); but probably due to reaction (6) which is supported by other workers [10] and also due to the reaction (equation 7), though it is claimed [10] that sulphate ion is stable at this potential. Such a process may be expected to provide an anodic peak around -0.14 V. Kelsal and Page [13] observed a reduction peak at -0.34 V and an oxidation peak at -0.19 V. It has been observed during polarisation in 2N  $H_2SO_4$  (Fig.4), a peak appears at 0.08V during anodic cycle and this may correspond to the oxidation of  $H_2S$ . In other cases it can be assumed that the rising portion of the curve in the forward or anodic cycle may be composed of  $ZnS$  and any adsorbed  $H_2S$  undergoing oxidation.

A peak in cathodic cycle has also been observed by Narasagoudar et al. [8] and they have attributed the decrease in current after 600 mV as observed in the present case to the reduction of  $Zn(OH)_2$  or  $ZnO$

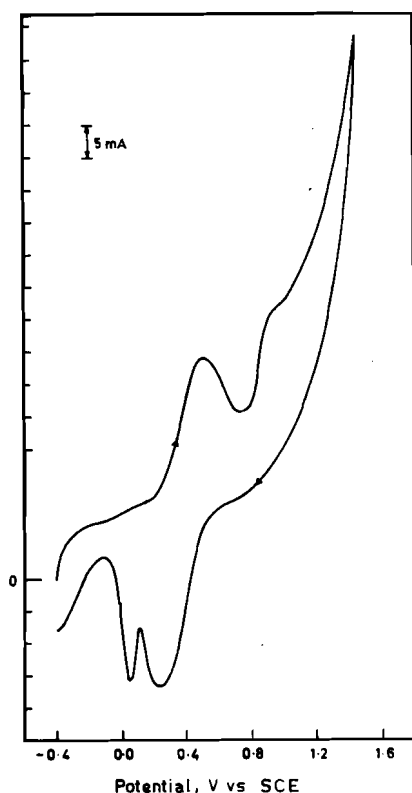
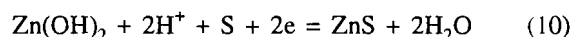


Fig.5: Cyclic voltammogram of sphalerite compact electrode in 1N  $H_2SO_4$ . Sweep rate  $5 \text{ mVs}^{-1}$ . Potential range -0.4 to 1.5V

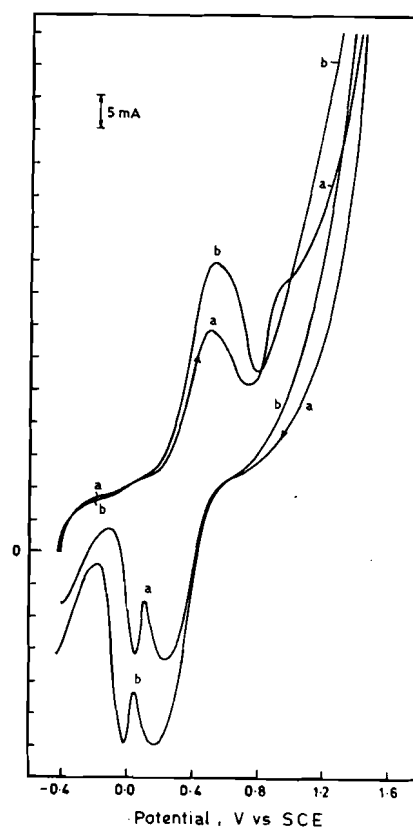


Fig.6: Effect of scan rate on voltammogram of sphalerite compact electrode in 1N  $H_2SO_4$ . a.  $5 \text{ mVs}^{-1}$ , b.  $10 \text{ mVs}^{-1}$

As in the case of  $H_2S$  sparging,  $ZnS$  produced by the reaction (equation 10) also is expected to be less conducting. Moreover it does not provide any reason for the increase in current in the subsequent cycle. The reduction of  $ZnO$  by  $H^+$  ions takes place at a much more negative potential ( $-0.68$  V).

### Effect of change of initial potential

It is seen from Fig.5 that a reduction appears near 0 V and also below 0 V. In order to have a complete picture of oxidation and reduction reaction below 0 V, the initial potential is changed to slightly cathodic i.e. to  $-0.4$  V and the final potential is kept at the same level i.e. at  $1.5$  V. It can be seen from the Fig.5 that two well defined peaks appear in the reverse cycle around a potential of  $0.15$  V ( $C_1$ ) and  $0.06$  V ( $C_2$ ). As already explained the peak at  $0.06$  V may be due to the reduction of sulphur to  $H_2S$ . It can be seen that after the second peak the current becomes less cathodic and crosses zero and becomes anodic. This may be due to the adsorption of  $H_2S$  formed on the electrode thereby preventing the further reaction. After a potential of  $-0.1$  V, the current again becomes cathodic and it may be due to the reduction of  $ZnO$  or  $Zn(OH)_2$ .

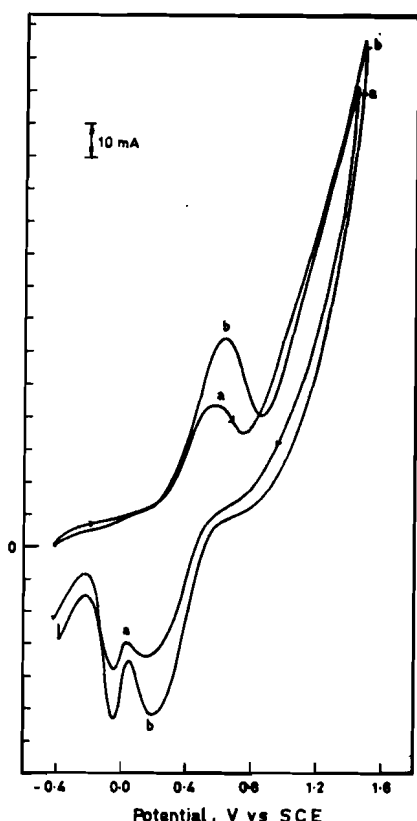


Fig.7: Effect of scan rate on voltammogram of sphalerite compact electrode in  $1$  N  $H_2SO_4$ . a.  $20$ , b.  $50$   $mVs^{-1}$

### Effect of scan rate

As the scan rate is increased from  $5$   $mVs^{-1}$  to higher values (maximum scan rate =  $200$   $mVs^{-1}$ ), peak currents increase and also the tendency of the current changing from cathodic to anodic becomes less. Except for  $5$   $mVs^{-1}$  sweep rate, all curves taken at higher scan rates remain cathodic after second cathodic peak and their cathodic peak currents increase with the scan rates. These are presented in Figs.6 and 7. The reason may be due to less adsorption of  $H_2S$  on the electrode surface because of faster scan rates. Also there is a slight increase in the anodic peak current when the initial potential is changed from  $0$  V to  $-0.4$  V (At  $20$   $mVs^{-1}$  scan rate the  $i_p = 33$  mA when initial potential is  $0$  V. It increases to  $35$  mA when initial potential is changed to  $-0.4$  V).

### CONCLUSION

Cyclic voltammetric studies with compacted sphalerite electrodes show that during anodic oxidation of  $ZnS$  the main products are sulphur and sulphate which undergoes reduction to  $H_2S$  during reverse cycle.

By changing initial potential to  $-0.4$  V the study shows two well defined peaks in the reverse scan due to the reduction of sulphur to  $H_2S$ .

The increase in the scan rate produces higher anodic currents and the tendency to remain cathodic also decreases. The cathodic peak currents also increase with scan rates.

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