

Concentration effects of hydrochloric acid on the anodic behaviour of lead sulphide

B. DANDAPANI, E. GHALI

Department of Metallurgy, Laval University, Québec, Canada G1K 7P4

Received 27 July 1981

The anodic dissolution of lead sulphide is studied at various chloride concentrations and at different pH values. At 25°C it is found that in hydrochloric acid the dissolution rate reaches a maximum around 3.0 mol dm⁻³. It has also been observed that at concentrations between 0.7 and 1.2 mol dm⁻³, a crystalline sulphur deposit formed during the dissolution process leads to an independent peak on the *I-E* curve whereas at higher concentrations it merges with the PbCl₂ peak formation. pH has no significant effect on the dissolution rate. The results of a systematic study on the kinetics of the dissolution process as a function of concentration, temperature and pH are discussed.

1. Introduction

The choice of an aqueous medium for the electro-dissolution of lead sulphide is restricted due to the very limited solubilities of the lead salts formed during the process. In alkaline solutions the final products always tend to be the oxides of lead instead of the metal. Among the mineral acids, nitric acid is not suitable as it is highly oxidative in nature and the lead sulphate formed in a sulphuric medium has a very low solubility ($1 \times 10^{-8} = K_{sp} \text{PbSO}_4$) [1]. Hydrochloric acid appears to be a better choice since PbCl₂ is reasonably soluble [1], $K_{sp} 1 \times 10^{-4}$ at 25°C in water and slightly higher in HCl. Further, a chloride medium looks more promising for electro-dissolution studies of PbS due to the low overpotential required. Based on this information some preliminary studies made on the anodic behaviour of lead sulphide in hydrochloric acid has been reported earlier [2]. Further systematic studies of the anodic behaviour of PbS as a function of concentration of chloride, pH and temperature are presented here.

2. Experimental procedure

2.1. Electrodes and chemicals

The lead sulphide electrode is prepared by fusing 99.9% lead sulphide powder (supplied by Alfa Products) and casting in a boron nitride mould.

The details of the preparation method are described elsewhere [3]. The electrodes were polished successively with 240-600 grit emery paper, washed thoroughly with distilled water, introduced into the electrolyte and polarized within 30 s.

2.2. Apparatus

A Tacussel PRT 20-2 potentiostat in combination with a Tacussel Servovit 9 function generator are used for the voltammetric studies. A Hewlett-Packard 7000 AM *X-Y* recorder and a digital voltmeter were used for recording the current potential curves and the potential measurements, respectively. Detailed descriptions of the electrochemical cell, experimental procedures etc. were given in an earlier report [2].

3. Results

The potentiodynamic anodic curves for PbS in hydrochloric acid at various concentrations from 0.3 to 0.8 mol dm⁻³ are shown in Fig. 1 and those from 0.9 to 5.0 mol dm⁻³ in Fig. 2. The scan rate is 10 mV s⁻¹. It is seen from Figs 1 and 2 that the rate of dissolution (shown by peak B) increases with the concentration of the acid upto 3.0 mol dm⁻³ but then falls off with a further increase in acid concentration. The increase in the dissolution rate with concentration is similar to the observation of Barradas *et al.* [4] in their electrochemical

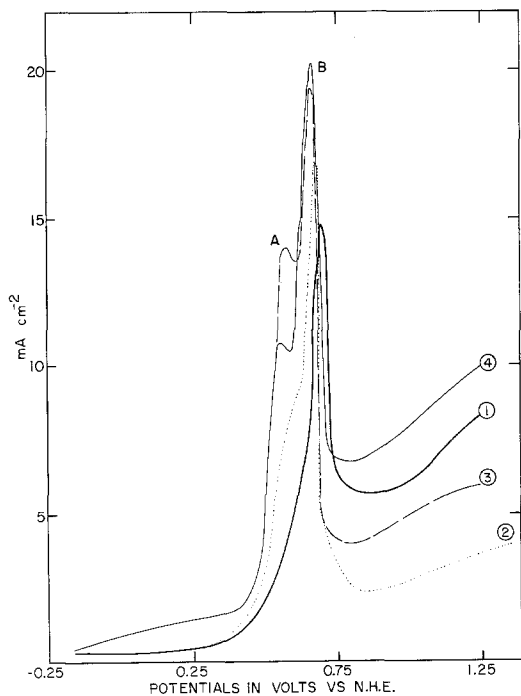


Fig. 1. Concentration effects on the anodic dissolution of PbS in HCl at 600 mV min^{-1} and 25°C . (1) 0.3 , (2) 0.5 , (3) 0.7 and (4) 0.8 mol dm^{-3} HCl.

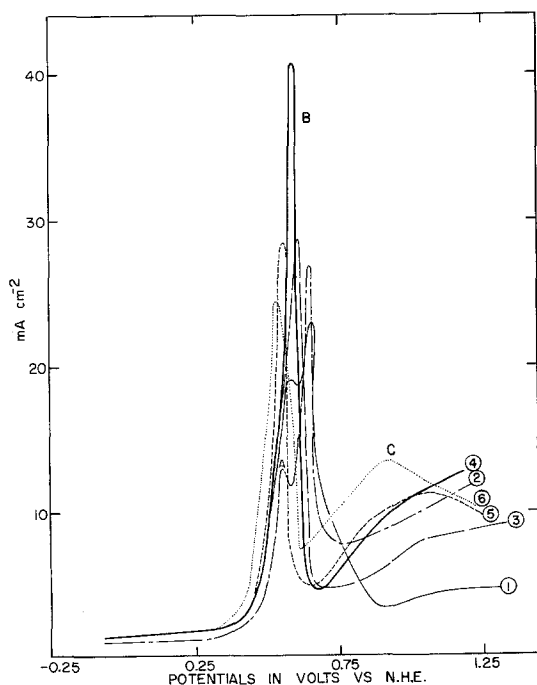


Fig. 2. Concentration effects on the anodic dissolution of PbS in HCl at 600 mV min^{-1} and 25°C . (1) 0.9 , (2) 1.0 , (3) 2.0 , (4) 3.0 , (5) 4.0 and (6) 5.0 mol dm^{-3} HCl.

studies of lead in HCl. However, they have not observed a maximum dissolution at an intermediate concentration. It can be observed that a shoulder peak (A) develops at about 0.7 mol dm^{-3} HCl but at a concentration of 1.2 mol dm^{-3} and beyond where this peak merges with the main peak B. This shoulder/peak is also sensitive to an increase in temperature. Even at 1.0 mol dm^{-3} HCl, peak A is not observed above 40°C [5]. To define the nature of the product formed at the potential of peak A, a surface analysis of the electrode polarized to this potential at various temperatures upto 80°C has been made. Fig. 3 shows two typical scanning electron micrographs of such a surface, taken at two different sites (on the same surface) on an electrode polarized at 60°C . Moreover X-ray diffraction studies identify the presence of elemental sulphur both in crystalline and globular form spread sporadically over the polarized surface. Peak B was established earlier to be due to PbCl_2 formation. The third peak (C) is also highly dependent on the concentration of acid, sweep rate and temperature. This peak is not clearly resolved until a concentration of 4.0 mol dm^{-3} is reached at 25°C but it could be seen at a concentration of 1.0 mol dm^{-3} when the sweep rate was reduced to 100 mV min^{-1} . It is also seen at 600 mV min^{-1} in 2.0 mol dm^{-3} HCl when the temperature is increased to 50°C . The effect of temperature can be seen from the curves for different HCl concentrations at 80°C shown in Fig. 4. It is clearly seen that the corrosion rate increases with the temperature and concentration of the acid. At a concentration of 5.0 mol dm^{-3} , peak C alone is observed. X-ray diffraction studies of the surface products show that the formation of PbSO_4 is responsible for peak C.

To confirm the higher dissolution rate of PbS with an increase in the HCl concentration and temperature, potentiostatic studies were conducted in the potential region of peak B in 5.0 mol dm^{-3} HCl at 25 and 80°C . The $i-t$ curves are shown in Fig. 5: The continuous decrease in current with time indicates that the products of the reaction accumulate on the surface to act as a passivating layer. However, due to poorer adhesion of the products or higher solubility at 80°C the steady current at this temperature is considerably higher than at 25°C even after 7 h. When analysed by X-ray diffraction the

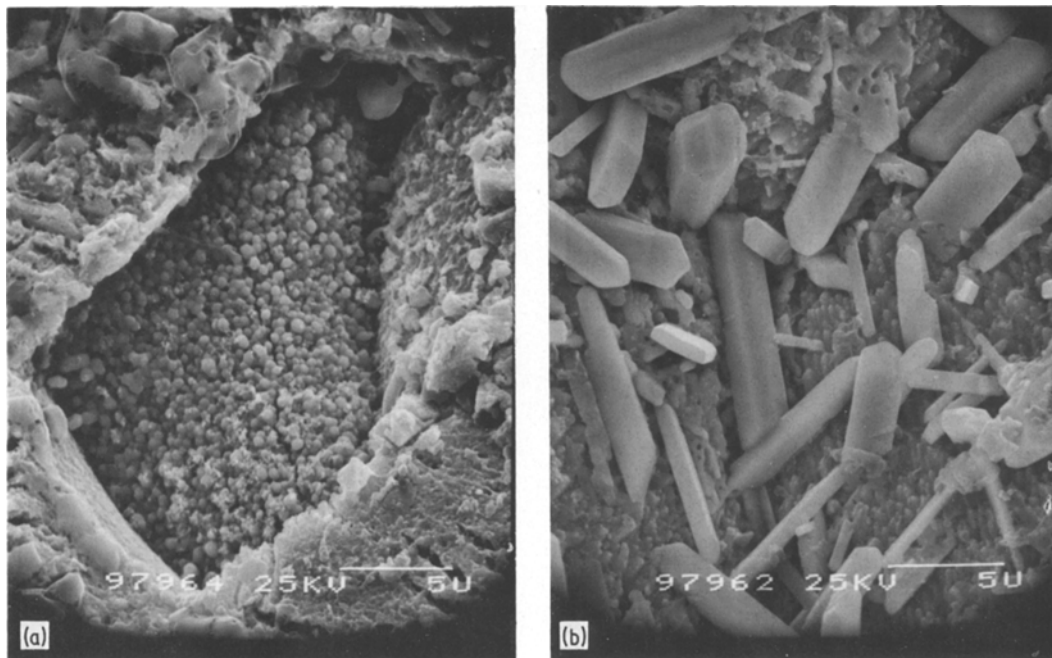


Fig. 3. Scanning electron micrographs of a PbS surface polarized to peak A potential. $\times 4000$. (a) and (b) represent two different sites on the same surface.

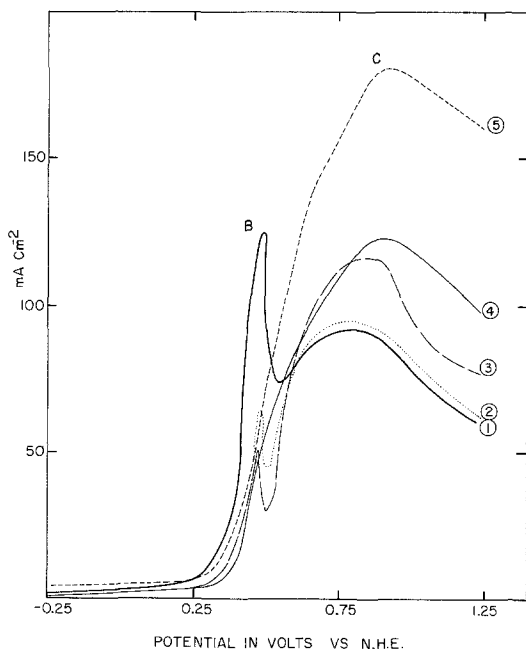


Fig. 4. The anodic dissolution curves of PbS at various concentrations of HCl at 80°C . Sweep rate 600 mV min^{-1} . (1) 1.0 , (2) 2.0 , (3) 3.0 , (4) 4.0 and (5) 5.0 mol dm^{-3} HCl.

products deposited on the surface at the end of the experiment confirmed the presence of elemental sulphur, lead chloride, lead sulphate and unreacted lead sulphide.

The effect of pH on the dissolution rate at 25°C with 1.0 and 3.0 mol dm^{-3} chloride concentrations is shown in Fig. 6 a and b. The results are in accordance with the expectations, i.e. the dissolution rate decreases and peak B shifts towards a more noble potential with an increase in pH.

4. Discussion

Two distinct observations made from Figs 1 and 2 are (a) the appearance of peak A around 0.7 mol dm^{-3} and (b) a maximum in the rate of PbS formation (peak B) at around 3.0 mol dm^{-3} HCl.

The appearance of peak A as a separate process starts at a concentration of 0.7 mol dm^{-3} HCl and merges with peak B at about 1.2 mol dm^{-3} . (The curve for 1.2 mol dm^{-3} HCl is not shown in Fig. 2 as it is very similar to that of 2.0 mol dm^{-3} with a peak current value a little higher than that of 1.0 mol dm^{-3}). It could be added that peak A is very prominent and is well resolved at a sweep rate

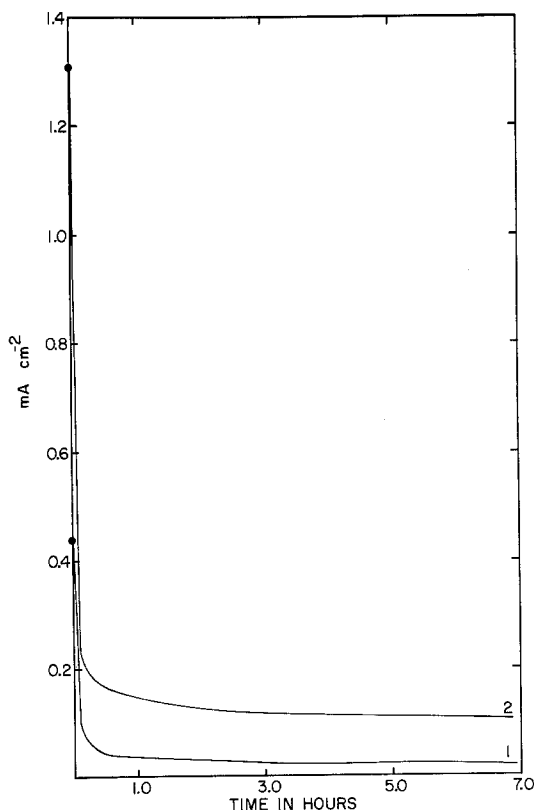
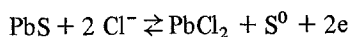


Fig. 5. Current-time curves for PbS at +0.74 V in 5.0 mol dm⁻³ HCl. (1) 25°C, (2) 80°C.

of 10 mV min⁻¹ in 1.0 mol dm⁻³ HCl [5].

Peak B in Fig. 2 indicates that the rate of anodic dissolution of lead sulphide increases with the concentration of HCl reaching a maximum around 3.0 mol dm⁻³. A further increase in concentration is seen to reduce the dissolution rate at 25°C. Normally we would expect the dissolution rate to increase steadily with increasing concentration (without reaching a maximum) due to the common chloride ion effect [6] and formation of lead chloride complexes [7]. This was the case for the dissolution of lead metal in hydrochloric acid [4] and lead chloride in sodium chloride solutions [8]. However, lead sulphide does not seem to fit this pattern of behaviour during its anodic dissolution. In this case the sulphur produced in the main reaction:



could play a part in reducing the dissolution rate by partially passivating the corroding surface. Surface studies of the polarized electrode through

scanning electron microscopy-energy dispersive X-ray analysis and X-ray diffraction studies [9] have shown that the sulphur produced in the above reaction contributes significantly to the passivation of the surface. The elemental sulphur formed is found to play a major part in reducing the dissolution of PbS beyond a certain concentration of HCl. This view is further substantiated by the observation that the dissolution does not reach a maximum but continues to increase with the concentration when the temperature is increased.

It has been found that an increase in temperature causes an increase in the dissolution rate of PbS. However, upto a concentration of 5.0 mol dm⁻³, peak C for PbSO₄ film formation exists at all temperatures indicating the very low solubility of PbSO₄ in HCl even at high temperatures (80°C). Also the passivation due to PbCl₂ is seen at all temperatures upto a concentration of 3.0 mol dm⁻³ HCl, and upto 60°C in 4.0 mol dm⁻³ HCl [5]. Passivation due to PbCl₂ is not seen in 5.0 mol dm⁻³ HCl beyond 25°C. This is very encouraging as the use of 5.0 mol dm⁻³ HCl and a high temperature will permit a high rate of PbS dissolution and extraction of Pb from PbCl₂ solution in HCl.

It is worthwhile at this stage to comment on the interesting phenomenon observed in 1.0 mol dm⁻³ HCl with increasing temperature. As mentioned earlier, the shoulder (peak A) results mainly from the crystalline nature of the sulphur formed on the surface during the dissolution process. As the temperature is increased, this shoulder is not observed above 40°C [5]. However, at the potential of this peak the sulphur formed does adhere to the surface in spite of the non-resolution of the peak A. Surface analysis of the electrode polarized to this peak potential at different temperatures indicates the presence of rhombohedral crystalline sulphur spread sporadically over the surface in addition to the globular form (Fig. 3a and b). Normally one would expect at temperatures of 60°C and above, that sulphur will be formed only in globular form. Interestingly enough at all temperatures upto 80°C rhombohedral crystalline sulphur could be identified on the polarized surface.

Based on the observations of (a) maximum dissolution rate at 3.0 mol dm⁻³ HCl, (b) non-resolution of peak A (at certain sweep rates in

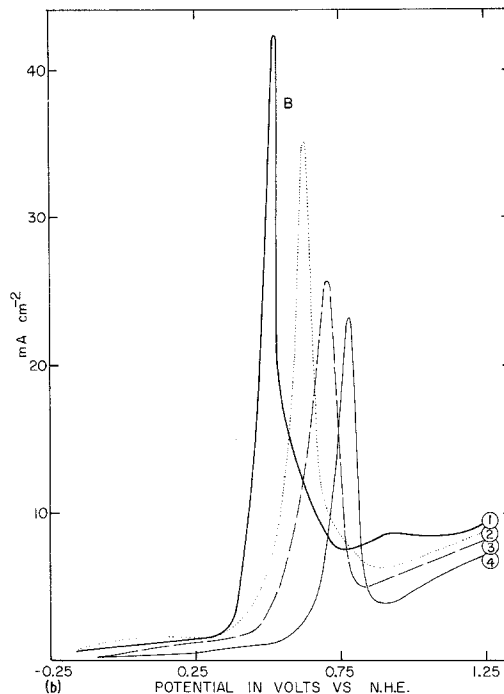
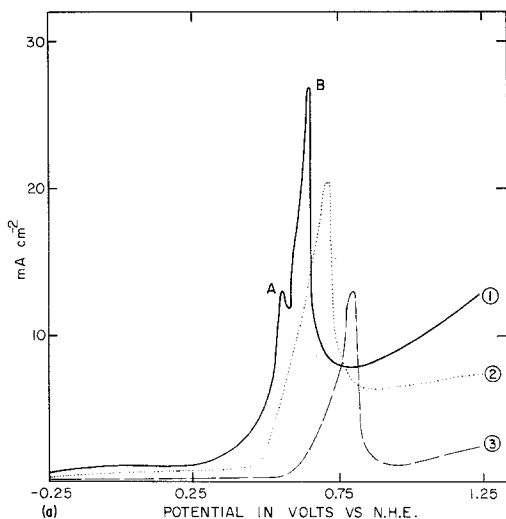
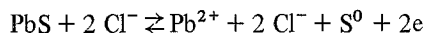


Fig. 6. (a) Effect of pH in $1.0 \text{ mol dm}^{-3} \text{ Cl}^-$ solutions at 25° C . Sweep rate 600 mV min^{-1} . (1) pH 0, (2) pH 3.0 and (3) pH 5.0. (b) Effect of pH in $3.0 \text{ mol dm}^{-3} \text{ Cl}^-$ solutions at 25° C . Sweep rate 600 mV min^{-1} . (1) $3.0 \text{ mol dm}^{-3} \text{ HCl}$, (2) pH 0, (3) pH 3.0 and (4) pH 5.0.

1.0 mol dm^{-3}) (c) the presence of crystalline sulphur on the surface even during dissolution at high temperatures and (d) identification of elemental sulphur mixed with PbCl_2 on the surface, could lead to the conclusion that peak B is due to the formation of a passive barrier consisting of sulphur rather than PbCl_2 . If PbCl_2 alone is responsible for the passivation peak B then one would expect a progressive increase in the dissolution rate [4, 8] with the concentration of the acid. In the present case sulphur acts as a barrier to the continuous dissolution of the PbS surface; the diffusion of the electrolyte is controlled by the structure of the passive layer. However, dissolution occurring beyond peak B could be due to a general corrosion restricted by the diffusion of the electrolyte to the surface, concentrated attack of the surface sites (where the passive layer is not fully covering the surface) causing pitting (as in Fig. 3a) or corrosion in the crevices. In effect the dissolution at and after peak B is completely diffusion controlled, the passive layer acting as a diffusion barrier.

Further, the dissolution maximum observed at 25° C in $3.0 \text{ mol dm}^{-3} \text{ HCl}$ does not persist when the temperature is raised. The continuous increase in the dissolution rate of PbS with temperature and the absence of peak B in $5.0 \text{ mol dm}^{-3} \text{ HCl}$

at 80° C suggests that the dissolution of the lead sulphide occurs by the reaction:



or by the formation of soluble complexes such as PbCl^+ , PbCl_2^0 or PbCl_3^- .

Among these PbCl^+ is the most soluble especially at high temperatures [7]. It may be that the diffusion barrier due to the reaction products, lead chloride and sulphur, is not effective enough, at higher temperatures, to obstruct the dissolution of the surface and this leads to the absence of a maximum at intermediate concentrations.

Finally, the effect of pH is not very significant in either 1.0 or $3.0 \text{ mol dm}^{-3} \text{ Cl}^-$. The dissolution rate is seen to decrease with an increase in pH. The only notable feature that could be observed from Fig. 6 is that the dissolution maximum reported for $3.0 \text{ mol dm}^{-3} \text{ HCl}$ is seen at all pHs at $3.0 \text{ mol dm}^{-3} \text{ Cl}^-$ concentration in contrast to those of $1.0 \text{ mol dm}^{-3} \text{ Cl}^-$ at the same pH values.

5. Conclusions

(1) The rate of dissolution of PbS in HCl at 25° C has been observed to reach a maximum at about $3.0 \text{ mol dm}^{-3} \text{ HCl}$.

(2) The observation of a maximum dissolution rate at 3.0 mol dm^{-3} HCl does not persist when the temperature is increased. A continuous increase in the dissolution rate with HCl concentration as well as temperature is then observed.

(3) The kinetics of the dissolution of PbS in HCl appear to be completely controlled by diffusion through a passive layer of the dissolution products, i.e. the lead chloride and sulphur which act as a diffusion barrier.

Acknowledgements

The authors are thankful for financial support of the work through a grant from the National Sciences and Engineering Research Council of Canada.

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