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Electrolysis of molten salt solutions containing PbSO$_4$

II. Products formed when using a carbon anode

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The anode products formed when electrowinning lead from lead sulphate dissolved in LiCl–KCl eutectic have been determined when using a carbonaceous anode.

Results indicate that electrolytic decomposition proceeds by the overall reaction

$$PbSO_4+C \rightarrow Pb+CO_2+SO_2$$

However at low current densities the CO_2 content increases by the reaction

$$C+SO_2 \rightleftharpoons CO_2+\frac{1}{v}S_v$$

The secondary reactions of the cathodically produced lead also increase the CO_2 and sulphur yields according to the following overall reactions

$$2PbO+C \rightarrow 2Pb+CO_2$$

and

$$PbS \rightarrow Pb+\frac{1}{v}S_v$$

All the above electrochemical reactions are extensively polarized and chlorine co-evolution starts at low current densities.

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1. Introduction

This study of the electrolysis products from carbonaceous anodes in lead sulphate–lithium chloride–potassium chloride melts was carried out in parallel with the cathode reaction study.

In pure sulphate melts the anion discharges two electrons forming sulphur trioxide and oxygen at currents above 1·0 mA cm^{-2} when an inert anode is used [2, 3, 4, 5, 6]. For example, Burrows and Hills [6] have shown that at oxidised platinum anodes the decomposition may be represented by the equations

$$Pt(O)+SO_4^{2-} \rightleftharpoons Pt(O).O+SO_3+2e \quad (1)$$

$$2Pt(O)O \rightleftharpoons 2Pt(O)+O_2 \quad (2)$$

where the first equilibrium is rate determining.

However, platinum and other electrodes that are normally inert are unsuitable for use in systems containing both sulphates and chlorides because of their tendency to be corroded under anodic potentials. For electrowinning lead, the sulphate–chloride system has advantages over pure sulphate melts with regard to corrosion,

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vapour pressure, temperature range, cathode efficiency and the tendency to dissolve by-products [1, 7]. The most suitable consumable anode material in sulphate melts is carbon, since its likely electrochemical and chemical decomposition products, CO_2 and/or CO, should not contaminate the melt. This is a possible alternative anode material in the absence of suitable non-consumable electrodes.

Earlier studies of graphite anode reactions in sulphate–chloride systems are not in complete agreement. Gul'din and Buzhinskaya [8] detected only SO_2 and CO_2 as the anode products, but they used an analytical technique which is expected to yield erroneous results when chlorine is present in the gaseous product. Liteanu and Cordos [9] also reported that only SO_2 and CO_2 were formed at the anode during the electrolysis of calcium sulphate–chloride melts, but they did not describe their analytical technique. L'vovich *et al* [10] showed that mixtures of SO_3, SO_2, CO_2 and CO were produced during electrolysis of sodium sulphate–sodium chloride systems, in the following proportions at 850°C:

SO_3 3– 5%
SO_2 45–55%
CO_2 25–35%
CO 8–18%

The principles involved in their method of analysis were not described although they did report that there was no chlorine evolution. An infra-red gas analyser was used by Arvia *et al* [11] to show that during electrolysis of bisulphate systems with graphite electrodes, SO_3, SO_2, CO_2 and CO were formed at temperatures up to 300°C. Shams el Din [12] indicated, but did not prove by analysis, that sulphates might constitute 'indifferent electrolytes' when added to chloride systems, which then became suitable for studying the concentration polarisation for chlorine evolution at the anode. This is contrary to the electrochemical series for the reduction of various anions in chloride melts when using carbonaceous electrodes. Rempel and Malkova [13] placed the anions in the following order of increasing cell voltage in a NaCl–KCl solvent at 700°C:

$$OH^-, NO_3^-, S^{2-}, SO_4^{2-}, Cl^-.$$

This series also indicates that at least one of the anions that may arise from reaction between the melt and the cathodically deposited lead [1, 7] (i.e., sulphide) would be electroactive in the sulphate–chloride system.

The aim of the present experimental study was to gain a better understanding of anode reactions that occur when electrolysing lead sulphate dissolved in a molten lithium–potassium chloride eutectic mixture under conditions in which lead is the cathode product.

The experimental approaches used were: to determine the effects of added oxides, sulphides and pyrosulphates on the cell reaction using voltammetry; To determine the composition of the anode product when purified systems were electrolysed under conditions of varying temperature, sulphate concentration and current density.

2. Experimental

Potentiostatic and galvanostatic parameters were fixed using standard instrumentation. For prolonged electrolyses, cell conditions were continuously monitored with a Solartron Data Logging Unit. The voltammetric study was carried out by varying the anode potential (5 mV s^{-1}) and recording the curves on an X–Y plotter.

The electrolyses were carried out in alumina and alumino-silicate cells. Spectroscopically pure graphite rods which were sheathed with alumino-silicate tubes (except at the working surfaces) were used as electrodes. The LiCl–KCl solvent melts were carefully purified before use. In the first series of measurements the reagent grade lead sulphate was found to have a significant nitrate content and this affected the shape of the voltammogram (as is illustrated in Fig. 1). Where necessary the nitrate could be removed by heating the reagent grade $PbSO_4$ with concentrated sulphuric acid.

Initially, gas analyses were carried out using gas-liquid chromatography and redox tests of sodium hydroxide absorbing solutions. A multiple end point potentiometric titration technique was then devised to analyse the absorbing solutions quantitatively. The method involved treating aliquots with iodine or iodide ions, depending on the presence of excess chlorine (hypochlorite) or sulphur dioxide (sulphite) in the solutions, followed by silver nitrate titration. Carbon dioxide (carbonate) was determined by acidimetric titration of a separate pretreated aliquot.

3. Results and Discussion

3.1 *Current-voltage curves*

Current-voltage curves were measured so that the number of electrode processes occurring could be determined and also to find the approximate potentials at which they occurred. The reacting anions were identified by a concentration reinforcing method.

Curve I of Fig. 1 is a typical curve for a freshly prepared melt using purified LiCl-KCl eutectic and pure $PbSO_4$ at 700°C. Three separate decompositions are evident from the curve. The low potential process A_I commenced at approximately 0·2 V and this was shown by concentration reinforcement to be oxide decomposition (see Fig. 2). The second process B_I, commenced at approximately 0·7 V with a further change in electrode process occurring at a current density of approximately 50 mA cm^{-2} (or 1·2 V). The second process was shown to correspond to sulphate decomposition by concentration reinforcement as is illustrated by curve II of Fig. 1. The high potential process C_I is deduced to be chloride ion decomposition after elimination of the effects of the presence of oxide and sulphide ions and from subsequent analyses of off gases.

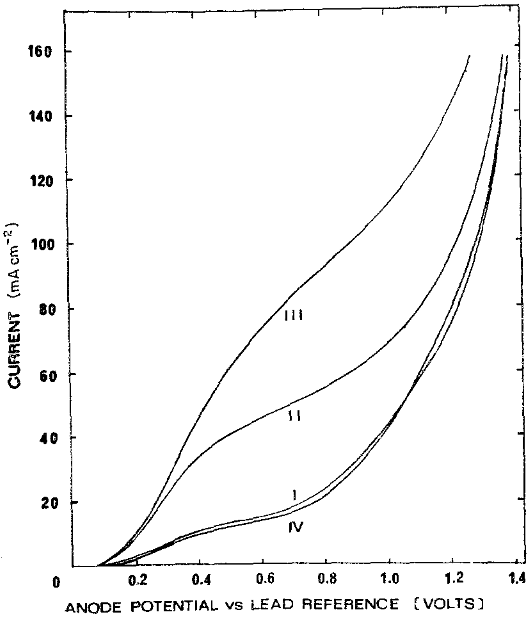

Fig. 2. Influence of PbO on current-anode potential (versus lead reference) curves for $PbSO_4$ in LiCl-KCl eutectic at 700°C. Curve I—2 mole % reagent grade $PbSO_4$. Curve II—2 mole % reagent grade $PbSO_4$+0·5 mole % PbO. Curve III—2 mole % reagent grade $PbSO_4$+1 mole % PbO. Curve IV—1 mole % reagent grade $PbSO_4$+1 mole % PbO+2 mole % $K_2S_2O_7$.

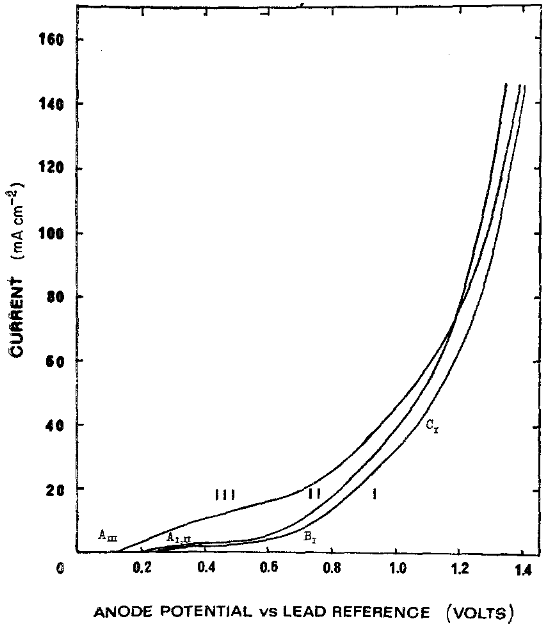

Fig. 1. Current-anode potential (versus lead reference) curves for $PbSO_4$ in LiCl-KCl eutectic at 700°C. Curve I —2 mole % acid digested $PbSO_4$. Curve II—5 mole % acid digested $PbSO_4$. Curve III—2 mole % reagent grade $PbSO_4$.

Curve III of Fig. 1 illustrates the effect of the presence of impurities in reagent grade lead sulphate (prior to sulphuric acid digestion). The small current observed in process A_{III} is due to electrolytic decomposition of lead oxide which arises from thermal decomposition of the nitrate content of the reagent grade lead sulphate as the sample is heated. Nitrogen dioxide evolution was observed during the melt fusion. Corrosion reactions or acid-base decomposition of $PbSO_4$ could be responsible for the low potential processes A_I and A_{II}, since these processes would form small amounts of lead oxide or basic lead sulphate also.

The change in shape of the current-voltage curve when lead oxide additions are made is illustrated in Fig. 2. Further proof that oxide ion discharge is responsible for the low potential process was furnished by additions of potassium pyrosulphate, which diminished the low potential currents (curve IV, Fig. 2) in accordance with the reaction

$$S_2O_7^{2-} + O^{2-} \rightarrow 2SO_4^{2-} \qquad (3)$$

Flood and Forland [14] have shown that the equilibrium of this process is strongly displaced to the right under conditions similar to those used here.

Reaction between the cathode products and lead sulphate of the melt has been found to give rise to lead sulphide as well as lead oxide (or basic lead sulphate) during normal electrolysis. Therefore the effect of the presence of lead sulphide on the voltammogram is of interest in determining the anode products that would be formed during continuous electrolysis.

Additions of lead sulphide were made to freshly prepared sulphate–chloride melt systems with the results shown in Fig. 3. An additional decomposition is evident at approximately 0·1 V.

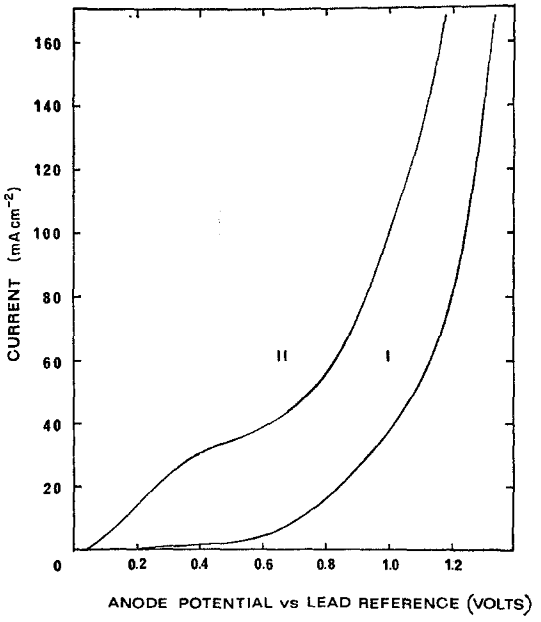

Fig. 3. Influence of PbS additions on current-anode potential (versus lead reference) curves for melts containing 5 mole % $PbSO_4$ in LiCl–KCl. Curve I—No sulphide present. Curve II—After adding 2 mole % PbS.

King [15] has shown that electrolysis of lead sulphides would commence at a voltage of less than 0·2 V at this cell temperature, with the formation of a polysulphide, and that sulphur evolution would become dominant at higher potentials.

Further additions of lead sulphide above 2 mole % caused no change in the shape of the current voltage curve, indicating that the lead sulphide solubility was less than this amount under the conditions of the experiment. This low solubility of PbS is expected from other studies [9, 10], the solubility being primarily dependent on the lead-chloride content of the melt.

3.2 *Decomposition voltages*

Numerous voltammograms have been recorded during the experimental study for lead sulphate solutions in the lithium chloride–potassium chloride eutectic mixture at concentrations 0·5–10·0 mole % and temperatures 550–720°C. The discharge potentials for the sulphate ion were obtained by extrapolation of the polarization curve to zero current except where an appreciable current flowed at potentials below the decomposition, when the curve was extrapolated to the current value at which the new decomposition commenced. These discharge potentials were then corrected to standard E^0 voltages using the Nernst equation and calculating the concentration term by the Temkin model for salt mixtures; values of E^0 so obtained are listed in Table 1.

The standard voltages determined are more consistent with the reaction

$$\begin{aligned} &PbSO_4 + C \rightleftharpoons Pb + SO_3 + CO \\ &\Delta G_{872°K} = 23.2 \text{ kcal}, \\ &E^0_{872°K,\ calc} = 0.503 \text{ V} \end{aligned} \qquad (4)$$

than with the sulphur dioxide formation reaction

$$\begin{aligned} &PbSO_4 + C \rightleftharpoons Pb + SO_2 + CO_2 \\ &\Delta G_{872°K} = -22.2 \text{ kcal}, \\ &E^0_{872°K,\ calc} = -0.5 \text{ V} \end{aligned} \qquad (5)$$

If the former reaction occurred, then oxygen, carbon monoxide, sulphur trioxide and sulphur dioxide would be present in off gases during galvanostatic electrolyses since sulphur trioxide is unstable in the temperature range of the

Table 1. Decomposition potentials for lead sulphate in LiCl–KCl eutectic

Temperature °*C*	*Conc.* $PbSO_4$ *(mole fraction)*	*E (measured) volts*	*E*°	*Mean E*°
550	0·005	1·15	0·87	
	0·01	1·13	0·91	
	0·05	1·02	0·91	
	0·10	1·00	0·93	0·91
600	0·05	0·85	0·72	
	0·10	0·80	0·73	0·73
620	0·005	0·84	0·54	
	0·010	0·75	0·50	
	0·05	0·78	0·66	
	0·10	0·80	0·63	0·59
680	0·005	0·70	0·40	
	0·05	0·60	0·47	0·44
700	0·005	0·82	0·50	
	0·01	0·78	0·60	
	0·02	0·70	0·50	
	0·05	0·53	0·40	0·50
720	0·05	0·56	0·42	0·42

experiments. In fact, as shown below, oxygen was never detected while carbon monoxide was only present in trace amounts as determined by gas liquid chromatography. The value of the thermodynamic comparison therefore becomes questionable, as is also emphasized by another apparent anomaly in the observed current-voltage curves. Lead oxide should react with carbon yielding CO_2, CO or mixtures of both gases, these reactions having negative free energy changes in the temperature range considered, yet the voltammograms suggest that positive free energy changes are associated with the reactions in practice. Similar current-voltage observations to those made here have been made by Steele [20] in the PbO–$PbCl_2$ system.

It has been suggested [1,16, 17] that the rate of electrochemical oxidation of graphite in fused salts is controlled by non-electrochemical steps which involve the desorption of carbon-oxygen intermediates at rates which are sensitive to the reaction temperature. Arvia [11] concluded that the electrochemical oxidation of graphite in bisulphate and nitrate melts was similar in nature to the chemical oxygenation reaction in this respect. Tucker and Mulcahy [18] showed that the rate of the desorption reaction during chemical oxidation was slow up to 600°C but then increased sharply. This latter observation is in line with the present experimental results where the current associated with both sulphate and oxide decomposition increased sharply with temperatures above 600°C.

Studies of cryolite–alumina–carbon systems at 1000°C [16, 17] have indicated that the primary source of anodic overpotential during electrolysis is the non-electrochemical desorption reaction. Similar behaviour was reported in KCl–NaCl–Na_2SO_4 systems at 650°C [21]. It therefore seems reasonable to sugges tthat the discrepancy between the observed and thermodynamically predicted current-voltage behaviour is at least partly due to the presence of a non-electrochemical slow step in the oxidation, and that the concepts of ‘reaction’ overvoltage [19] may be applicable in oxide and, more especially, sulphate decomposition at graphite anodes. The extrapolations made in this investigation would become inaccurate due to the extremely low exchange currents of the electrochemical processes involving formation of carbon oxides.

3.3 *Galvanostatic electrolyses*

To determine anode product compositions and carbon consumption data, electrolyses were run at temperatures of 500°C, 600°C and 700°C, anode current densities from 0·015 to 0·25 A cm^{-2} and lead sulphate concentrations of 2, 5 and 10 mole percent. Although considerable care was taken in the experiments, the results showed an undesirable amount of scatter. Analytical errors, gas leaks and cathode product back reactions were shown to be significant contributors to the observed scatter. The influence of back reactions, particularly of the lead, was shown to be of major importance by the formulation and testing of a mathematical model of the overall electrochemical cell [7]. After allowing for the effect of the back reaction of lead these results suggest that the overall cell reaction for electrolytic decomposition of lead sulphate is the same as suggested by Equation 5 above. This is shown by quantitative product analysis results (see Figs. 4, 5 and 6 which illustrate trends observed during the experiments). The bulk of the current passing could be accounted for in terms of the anode products SO_2, CO_2 and Cl_2 assuming the lead sulphate is decomposed by the above reaction.

In all cases carbon dioxide was present in excess over the level predicted from sulphur dioxide analysis, although the excess decreased as current density increased. The cathodic studies have shown that we would expect the steady-state concentration of PbO to increase as current density is lowered. This in turn would increase the amount of CO_2 formed (per mole of SO_2) by the electrochemical reaction

$$2PbO + C \rightarrow 2\,Pb + CO_2 \qquad (6)$$

becoming more important. It would not however cause the moles CO_2 per g atom of lead to exceed unity as is observed (Fig. 4) at low current densities.

This coulometric excess suggests then that CO_2 also arises from another reaction. The free energy change for the reaction

$$C + SO_2 \rightarrow CO_2 + S \qquad (7)$$

is negative at all temperatures studied, being −24 kcals at 650°C. If desorption of SO_2 from the electrode surface were slow, this reaction would be possible and would give rise to an increase in CO_2 over that theoretically expected while decreasing the amount of SO_2 formed.

This is further supported by the detection of traces of sulphur in some experiments although the sulphur could also have been formed from electrolysis of dissolved sulphides (see Section 3.1).

Increases in anode current density caused decreases in the oxide content of the products and an increase in the chlorine content. Critical current densities were observed below which chlorine was not evolved; the magnitude of the critical current density for chlorine co-evolution was increased by increasing the cell temperature and/or the lead-sulphate content of the melt, and by the accumulation of products associated with reactions of the cathodically deposited lead.

The CO_2/SO_2 ratio (Fig. 5) decreases to a minimum which is initially approached at the current density that coincides with the initiation of chlorine evolution. The value of the CO_2/SO_2 ratio appears to increase as the temperature is increased (Fig. 6) although the temperature dependence is not well defined. However, such a trend is expected if normal kinetic laws are obeyed. Certainly since the rate of formation

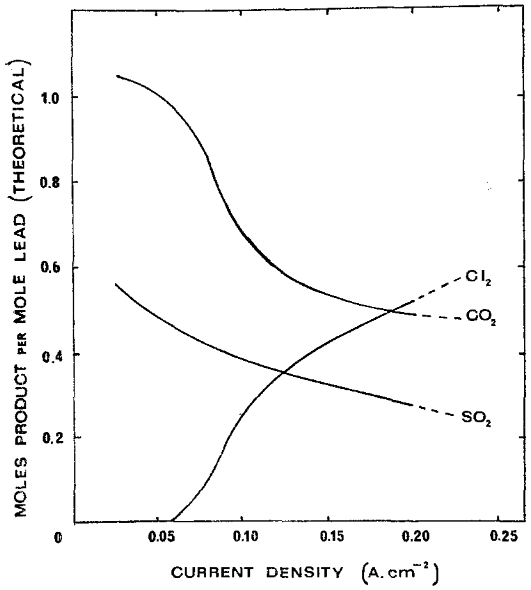

Fig. 4. Anode gas yields as a function of current density at 600°C. Melt: 5 mole % $PbSO_4$ in LiCl-KCl eutectic.

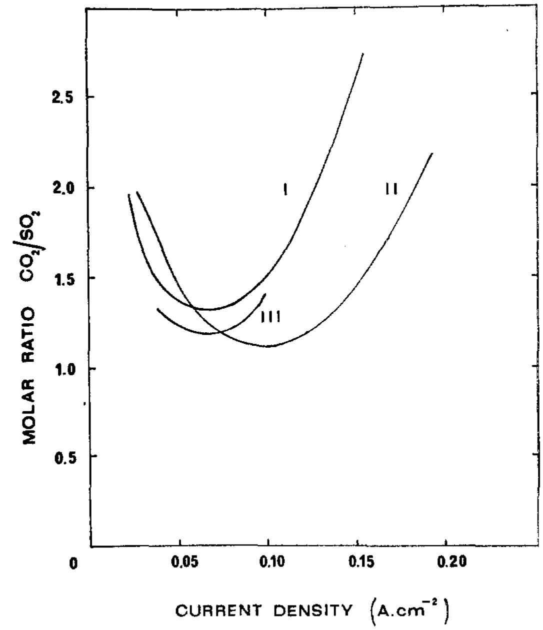

Fig. 5. Dependence of CO_2/SO_2 ratio on current density for various $PbSO_4$ concentrations at 600°C. Curve I—2 mole % $PbSO_4$. Curve II—5 mole % $PbSO_4$. Curve III—10 mole % $PbSO_4$.

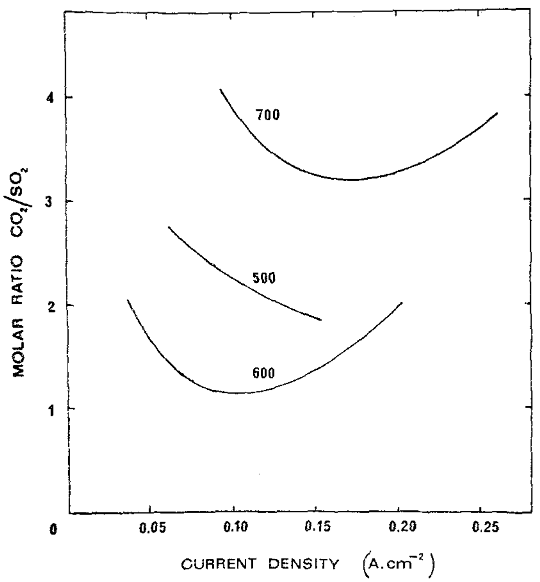

Fig. 6. Dependence of CO_2/SO_2 ratio on current density for various temperatures using 5 mole % $PbSO_4$ in LiCl–KCl.

of PbO increases with temperature we can explain the increase in CO_2/SO_2 ratio without making any assumptions on the rate of the reaction between SO_2 and carbon.

During the series of experiments performed, neither SO_3 nor O_2 were detected in any of the products analysed, although in some cases CO was present in trace amounts.

4. Conclusions and general discussion

By combining the results of the cathode studies with those presented above, a mechanistic picture of the overall cell reactions in a $PbSO_4$–LiCl–KCl system emerges.

Initially $PbSO_4$ will be electrochemically decomposed by the overall two electron transfer reaction given by Equation 5.

The anode reaction is accompanied by considerable polarization, but does not lead to a linear Tafel plot. Since only two electrons are transferred in forming a molecule of CO_2, an intermediate step involving a chemical reaction is probably involved in the overall anode process. For example, the anode mechanism for sulphate anion discharge may be

$$SO_4^{=} + C_s \rightleftharpoons C_sO + SO_{3(ads)} + 2e \qquad (I)$$

$$C_sO + SO_{3(ads)} \rightleftharpoons CO_{2(ads)} + SO_{2(ads)} \qquad (II)$$

$$CO_{2(ads)} \rightleftharpoons CO_{2(g)} \qquad (III)$$

$$SO_{2(ads)} \rightarrow SO_{2(g)} \qquad (IV)$$

The absence of SO_3 and O_2 indicates that step II, the chemical reaction, is quantitative. From the gas analysis (see Section 3·3 and Equation 7) it also appears that step IV is slow and the absorbed SO_2 undergoes a parallel reaction that contributes to the high carbon consumption.

Any lead oxide and lead sulphide formed by secondary reaction of the electrodeposited lead, will also be electrolytically decomposed.

At low current densities these reactions will predominate because of the greater relative amount of secondary reaction and the lower decomposition voltages of these materials. This is supported by the increase in CO_2/SO_2 ratio as the current density is lowered.

At higher current densities (or anode potentials) chlorine evolution commences, presumably due to electrolytic decomposition of lead chloride. When this occurs the CO_2/SO_2 ratio passes through a minimum with the proportion of CO_2 increasing again at higher anode potentials. The reasons for this increase have not yet been established.

The effect of increasing temperature is to lower the overpotentials of the electrochemical reactions and accelerate the reaction between SO_2 and carbon. This results in an increased carbon consumption but a lower chlorine evolution.

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References

[1] B. J. Welch and T. K. Hoa, This Journal—preceding paper.
[2] H. Flood and T. Forland, *Disc. Farad. Soc.*, **1** (1947) 302.
[3] C. H. Liu, *J. Phys. Chem.*, **66** (1962) 164.
[4] K. E. Johnson, and H. Laitinen, *J. Electrochem. Soc.*, **110** (1963) 314.
[5] A. J. Arvia, A. J. Calandra, and H. A. Videla, *Electrochim. Acta*, **13** (1968) 167.
[6] B. Burrows and G. J. Hills, *Electrochim. Acta*, **15** (1970) 445.

[7] R. A. Jenkins, M.Sc. Thesis, University of New South Wales (1971).

[8] I. T. Gul'din and A. V. Buzhinskaya, *Soviet Electrochemistry*, **1** (1965) 634.

[9] C. Liteanu and E. Cordos, *Rev. Roum. de Chimie*, **12** (1967) 985.

[10] F. I. L'vovich, S. A. Zaretskii and A. G. Morachevskii, *Zh. P.Kh.*, **40** (1967) 828.

[11] A. J. Arvia, W. E. Triaca and H. A. Videla, *Electrochim. Acta*, **15** (1970) 9.

[12] A. M. Shams el Din, *Electrochim. Acta*, **4** (1961) 242

[13] S. I. Rempel and E. M. Malkova, *Zh. P. Kh.*, **25** (1952) 558.

[14] H. Flood and T. Forland, *Acta Chem. Scand.*, **1** (1947) 781.

[15] P. L. King, Ph.D. Thesis, University of New South Wales (1971).

[16] J. Thonstad, *Electrochim. Acta*, **15** (1970) 1569.

[17] S. I. Rempel and L. P. Khodak, *Zh. P. Kh.*, **26** (1953) 931.

[18] B. G. Tucker and M. F. R. Mulcahy, *Trans. Farad. Soc.*, **65** (1969) 274.

[19] K. J. Vetter, 'Electrochemical Kinetics', Academic Press, New York (1967).

[20] R. J. Steele, Ph.D. Thesis, University of New South Wales (1971).

[21] S. I. Rempel, *Dokl Akad Nauk SSSR*, **117** (1957) 648.