Electrolysis of molten salt solutions containing PbSO$_4$

I. Reactions associated with the deposition of lead

TRAN KIM HOA* AND B. J. WELCH

School of Chemical Technology, The University of New South Wales, Kensington, N.S.W., Australia

Low faradaic yields of Pb were found when electrolysing melts containing PbSO$_4$ in solvents of either LiCl–KCl eutectic or Li$_2$SO$_4$–K$_2$SO$_4$–Na$_2$SO$_4$ eutectic and employing low current densities.

For all current densities employed, the decrease in current efficiency became greater as the lead sulphate concentration was increased but the influence of other sulphates was less pronounced.

From studies of the reaction of lead with the melt and a chronopotentiometric study of cathodic processes, we have found the following two reactions occur:
(a) Cathodic deposition of lead by the reversible reaction

$$Pb^{2+} + 2e \rightleftharpoons Pb$$
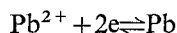
(b) Secondary non-electrochemical reaction of the electrodeposit

$$4Pb + 5PbSO_4 \rightarrow PbS + 4PbO.PbSO_4$$
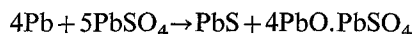
The rate of the latter reaction is sufficient to account for the lowering in current efficiencies. No evidence could be found to support direct reduction of the sulphate anion.

1. Introduction

The presence of sulphates in metallurgical reductions, such as used for the extraction of lead, is undesirable. Consequently there is a need for alternative extractive processes for some metals from the suphates. The results presented here are part of a practical study aimed at determining whether lead could be obtained from the electrolysis of lead sulphate in molten salt solutions. Because of the limited solubility of lead sulphate in aqueous solutions and the difficulty of preventing dendritic growth, aqueous electrolysis has met with limited success [1]. Earlier studies involving electrolysis of melts containing molten sulphates have lacked agreement about the cathode reaction [2, 3, 4], and therefore this practical study has some interesting implications.

* Present address: School of Chemistry, The University of New South Wales, Kensington, N.S.W. Australia.

Liu [2] found many metal ion-metal electrodes to be reversible in sulphates thus suggesting that the cathode reaction during electrolysis would be

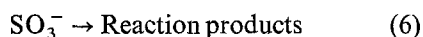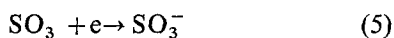$$M^{n+} + ne \rightleftharpoons M \qquad (1)$$
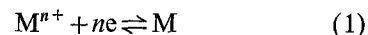
However analysis of the melt in the cathode compartment after electrolysis revealed both sulphite and sulphide in amounts which accounted for more than 95% of the electricity passed. This suggests that the cathode process is complicated and could involve the reactions

$$SO_4^{2-} + 2e \rightarrow SO_3^{2-} + O^{2-} \qquad (2)$$

$$SO_4^{2-} + 8e \rightarrow S^{2-} + 4O^{2-} \qquad (3)$$
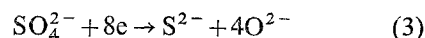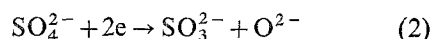
In another study Johnson and Laitinen [3] interpreted current voltage curves in molten sulphates to represent either the process given by Equation 1 or Equation 3. Differentiating between the two was difficult and they suggested

that it was influenced by the solubility of the oxides and suphides as well as the free energy of formation of the sulphates.

Senderoff [5] and Woodall [6] found that SO_4^{2-} could be directly reduced by a diffusion controlled two electron reduction when dissolved in molten LiCl–KCl. On the other hand Burrows and Hills [7] and Wrench and Inman [4] found that sulphate was not directly reduced in similar solutions. The latter workers suggested that readily reduced impurities such as water could account for the results of Senderoff and of Woodall. Wrench and Inman supported this by showing that in the presence of an oxide that is more acidic (according to the Lux–Flood acid-base definition) than SO_3, a cathodic process is introduced by the following reaction sequence:

$$MO_x + SO_4^{2-} \rightleftharpoons SO_3 + MO_{x+1}^{2-} \qquad (4)$$

$$SO_3 + e \rightarrow SO_3^- \qquad (5)$$

$$SO_3^- \rightarrow \text{Reaction products} \qquad (6)$$
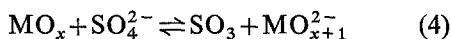
The general confusion about the cathode reaction, as indicated above, has also been reflected in the fragmentary interpretations of electrowinning studies previously carried out [8, 9, 10].

Gul'din and Buzhinskaya [8] used a lead cathode for electrolysing mixtures of Na_2SO_4–NaCl at 700°C. When interpreting their results, they assumed the cathode reaction to be
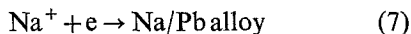
$$Na^+ + e \rightarrow Na/Pb\,\text{alloy} \qquad (7)$$

but they did not discuss its faradaic efficiency. However, L'vovich et al. [9] found that Na–Pb alloys reacted with Na_2SO_4–NaCl melts when the sulphate concentration exceeded 1% and cathode efficiencies (with respect to metal production) tended to zero. Similar observations were also made for $MgSO_4$–$MgCl_2$ mixtures [10].

It is evident from the above that we cannot confidently predict what products we would expect when electrolysing solutions containing molten lead sulphate. In the study reported here, two different solvents were used, namely the LiCl–KCl eutectic and the minimum melting composition of the ternary system Li_2SO_4–Na_2SO_4–K_2SO_4. The study involved the measurement of cathode efficiencies, reactions of lead

in the presence of the melt, and a limited chronopotentiometric investigation of the cathode process.

2. Experimental

The faradaic yields were determined by collecting, analysing and weighing the cathode product formed after the passage of an accurately measured amount of electricity. In the secondary reaction studies, the reaction of lead was followed by its weight loss as a function of time.

The electrolyses were carried out under an inert atmosphere using spectroscopically pure graphite electrodes and recrystallized alumina as a melt container, metal collection sheath, and insulator. Preliminary corrosion studies showed that both alumina and high alumina aluminosilicates were unaffected by the melt under all conditions used. Except for the differing materials of construction, the apparatus and procedure were similar to those described elsewhere [11].

The reacting lead for the secondary reaction studies was contained in a similar sheath to that used to collect the cathode product. It differed in the positioning of the melt circulation windows which were larger and extended down to near the metal-melt interface. For some studies a graphite screw stirrer was positioned adjacent to these windows.

Chronopotentiometry was carried out using standard procedures, the working or indicator electrode being a graphite rod insulated in a similar manner to the cathode described above. Potentials were measured against a second graphite rod which served as a quasi-reference electrode.

3. Results and discussion

3.1 Current efficiencies

The yield of lead was determined as a function of current density for each variable studied. Temperature dependence studies were conducted over the range 430°C to 680°C in a melt containing 4·4 mole % $PbSO_4$ dissolved in pre-purified LiCl–KCl eutectic. The assay of the metal produced indicated that it was pure lead (greater than 99·9% pure), and experimental results, as
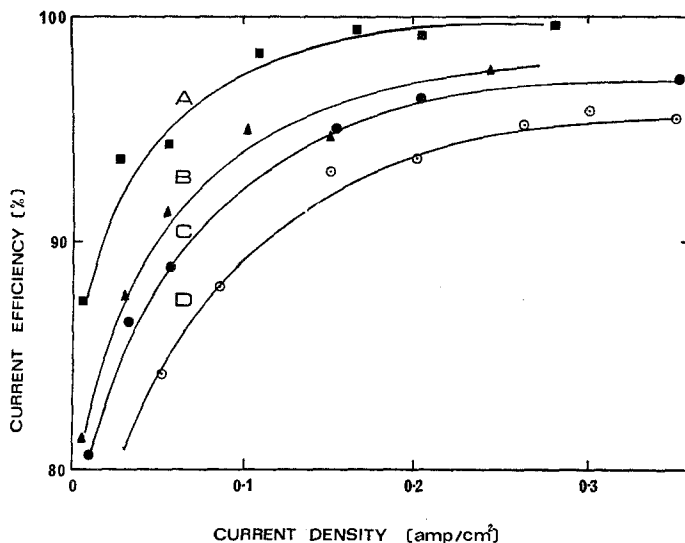
Fig. 1. The effect of current density and temperature on cathode efficiency. Melt: 4·4 mole % PbSO₄ in LiCl–KCl Curves: A (■) Temperature = 430°C; B (▲) Temperature = 480°C; C (●) Temperature = 550°C; D (☉) Temperature = 680°C.

expressed by current efficiency isotherms, are represented by Fig. 1.

Increasing the lead sulphate concentration causes a decrease in efficiency as is illustrated by the results presented in Figs. 2 and 3. In the latter case the chloride solvent was replaced by the ternary alkali sulphate mixture. A comparison of the two solvents for similar weight per-centages of lead sulphate, is also made in Fig. 3.

The shape of all current efficiency versus current density curves can be explained by either the deposited lead undergoing a secondary reaction or there being two cathode processes occurring. In the latter case however, the lower potential process would have a low limiting current and not give rise to lead. Because of the
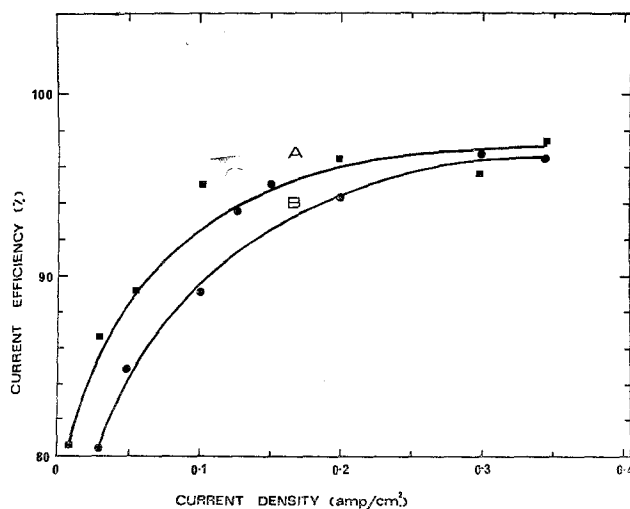

Fig. 2. The effect of lead sulphate concentration and current density on the cathodic current efficiency. Temperature = 550°C; A (■) 4·4 mole % PbSO₄ in LiCl–KCl; B (●) 5·8 mole % PbSO₄ in LiCl–KCl.
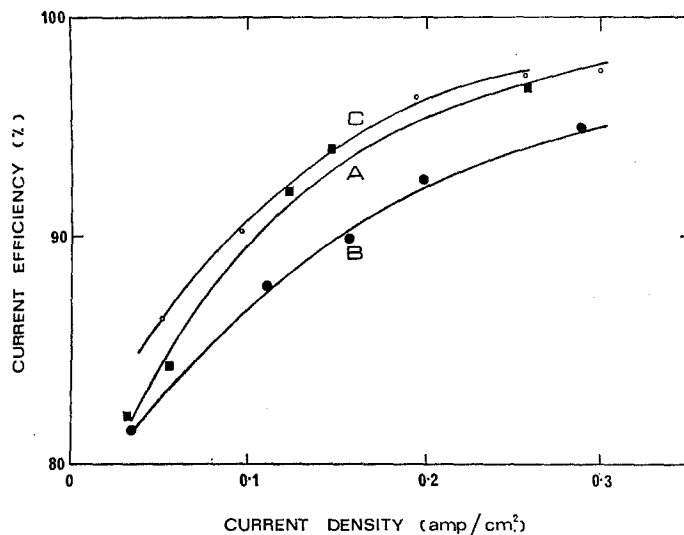
D

Fig. 3. The effect of melt composition on current efficiencies at 650°C;
A (■) 8·8 mole % PbSO$_4$ in Li$_2$SO$_4$–K$_2$SO$_4$–Na$_2$SO$_4$; B (●) 13·1
mole % PbSO$_4$ in Li$_2$SO$_4$–K$_2$SO$_4$–Na$_2$SO$_4$; C (○) 5·8 mole %
PbSO$_4$ in LiCl–KCl.

high lead yield and the continuous increase in efficiency with increased current density, the lead deposition reaction is the predominant one. The secondary process (i.e., that process that lowers the lead yield) increases with both temperature and lead sulphate concentration. It does not increase significantly, if at all, as the concentration of sulphate ions is increased at fixed lead ion concentration. This is indicated from comparing the results for the two different solvent systems under similar conditions where there is no significant difference in efficiency after allowing for the appropriate trends. Qualitatively this suggests that the secondary process is a reaction rather than an electrochemical reduction of the sulphate ion. If it were electrochemical and involved the sulphate ion as suggested by other workers [5, 6] we would expect the rate to be proportional to the sulphate ion concentration rather than the lead sulphate concentration, which is not indicated here.

Lead sulphide crystals were invariably present at the metal-melt interface in the experiments that involved the sulphate solvent. This suggests that the formation of a sulphide is a consequence of the process that lowers the metal yield.

3.2 Reaction of lead in the melts

A fixed weight of lead (approximately 3 g) was added to its containing sheath and this was immersed in the melt, by raising the crucible after thermal equilibrium had been attained, thus initiating the reaction. At the end of the desired reaction period the metal-containing sheath was removed and the metal remaining collected and weighed to determine the weight loss. Melt samples were also taken and analysed by chemical and X-ray diffraction procedures.

Initially results were obtained to determine the effect of mass transfer conditions. This was accomplished by comparing the rates of reaction when the melt was being stirred with those obtained when normal mass transfer conditions (i.e., no stirring) existed. No discernable difference was observed, and subsequent results were obtained with unstirred melts, thus maintaining similar mass transfer conditions to those existing for the current efficiency studies. The change in rate of reaction with temperature was studied over a similar temperature range, and for the same melt composition used for current efficiencies. The results presented in Fig. 4 show that lead loss is proportional to time and that the rate increases with temperature. Fig. 4 also shows that reaction rate increases as the lead sulphate concentration is increased indicating that either the sulphate anion or lead sulphate plays an important role in the dissolution of lead.

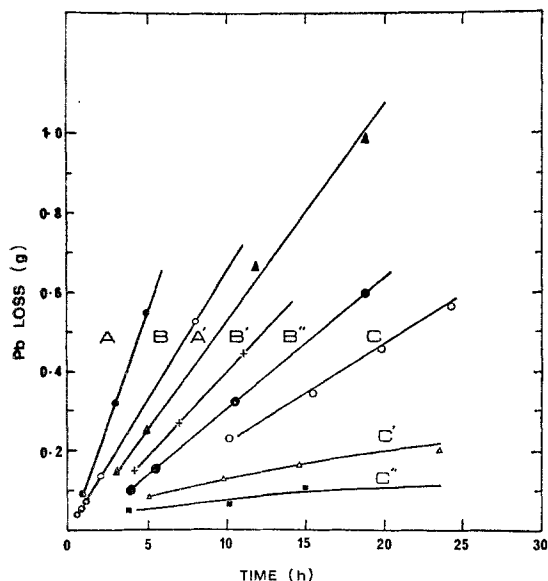The rate of dissolution of lead when the lead

Fig. 4. The reaction of lead with PbSO₄–LiCl–KCl melts. Curve: A (●) 21 mole % PbSO₄ at 800°C; A′ (▲) 21 mole % PbSO₄ at 500°C; B (○) 10·9 mole % PbSO₄ at 800°C; B′ (+) 10·9 mole % PbSO₄ at 700°C; B″ (●) 10·9 mole % PbSO₄ at 550°C; C (○) 4·4 mole % PbSO₄ at 600°C; C′ (△) 4·4 mole % PbSO₄ at 500°C; C″ (■) 4·4 mole % PbSO₄ at 430°C.

Fig. 5. The reaction of lead with PbSO₄–Li₂SO₄–K₂SO₄–Na₂SO₄ melts. Curve: A (●) 14·5 mole % PbSO₄ at 740°C; A′ (●) 14·5 mole % PbSO₄ at 600°C; A″ (●) 14·5 mole % PbSO₄ at 500°C; B (○) 8·8 mole % PbSO₄ at 740°C; B′ (○) 8·8 mole % PbSO₄ at 600°C; B″ (○) 8·8 mole % PbSO₄ at 500°C.

sulphate is dissolved in the ternary sulphate solvent (Fig. 5) is slightly higher than the rate when the chloride solvent is used. However plots of lead loss as a function of time tended to show more curvature for the sulphate solvent. This is probably due to the growth of lead sulphide crystals at the melt-metal interface which reduced the surface area for reaction. Lead sulphide crystals were invariably present at the metal surface when the starting melts contained only sulphates. In contrast, when the chloride solvent was used, there were no crystals formed at the interface although X-ray diffraction showed that lead sulphide was present in the melt phase.

Sulphides are fairly insoluble in sulphates [3]. The solubility of lead sulphide in LiCl–KCl melts is also low [12], but the solubility can be increased by the presence of lead chloride [13]. Therefore the absence of lead sulphide crystals in the chloride-sulphate system, but their presence in the melt can be explained by a fluxing action due to lead chloride produced by the exchange reaction
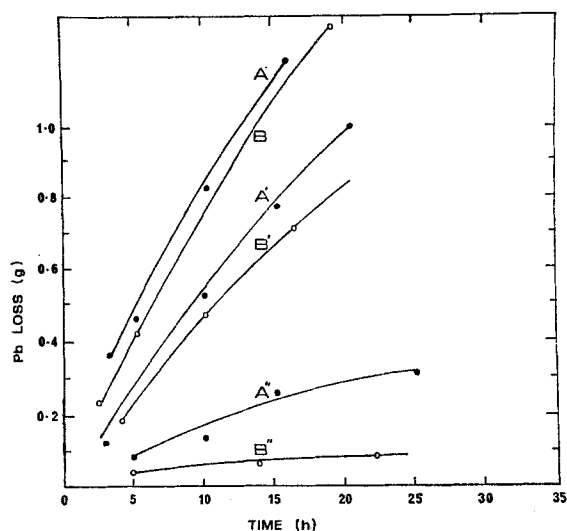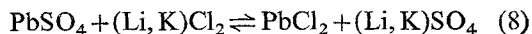
$$PbSO_4 + (Li, K)Cl_2 \rightleftharpoons PbCl_2 + (Li, K)SO_4 \quad (8)$$

Another reaction product found in all melts studied was PbO.PbSO₄. Kellogg [14] has shown that basic lead sulphates such as the one found here, are very stable entities at the temperatures used in this study.

The two reaction products suggest that the dissolution of lead proceeds via the following overall equation

$$Pb + 5PbSO_4 \rightleftharpoons PbS + 4 PbO.PbSO_4 \quad (9)$$
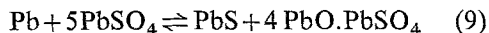
The standard Gibbs free energy change for this reaction is approximately −38 k cals at 600°C which further supports the proposed reaction.

3.3 Chronopotentiometric study

Various reviews of chronopotentiometry [15, 16, 17] have shown how the shape of the potential-time curve is related to the overall electrode reaction and its mechanism. Therefore it can be used as a diagnostic tool to assist in determining whether the loss in current efficiency is due to direct electrochemical discharge of the sulphate anion (see for example Equations 2 and 3) or the secondary chemical reaction as given by Equation 9 above.

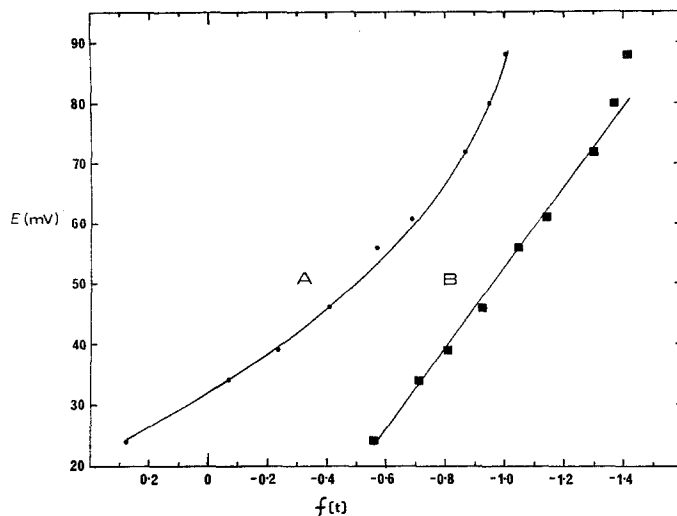The thermochemical data [14] suggests that if

Fig. 6. Potential-time relationship of cathodic chronopotentiogram of melt containing 1.56×10^{-4} mol cm^{-3} $PbSO_4$ in LiCl–KCl $\tau = 176$ ms; T = 410°C; $i = 0.70$ A; electrode area = 2 cm^2.

Curve A $f(t) = \log(\tau^{\frac{1}{2}}/t^{\frac{1}{2}} - 1)$

B $f(t) = \log(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})$

(Slope of curve B drawn = $RT/2F$).

the sulphate anion were electrochemically reduced, reduction would occur at a potential near or below that for discharge of lead ions (according to Equation 1) in the LiCl–KCl system when using carbon electrodes.

In this study cathodic chronopotentiograms were determined in the LiCl–KCl eutectic at 410°C using a graphite working electrode and $PbCl_2$, $PbSO_4$ or various mixtures of these two

salts (sometimes with added potassium sulphate) as the electro-active solute.

In all cases reduction commenced at a similar potential (0.88 V versus a graphite quasi-electrode) and the chronopotentiograms had similar shapes. The nature of these electro-reduction waves obtained for $PbCl_2$, $PbSO_4$ and mixtures of $PbCl_2 + PbSO_4$ was tested by plotting the potential versus $\log(\tau^{\frac{1}{2}}/t^{\frac{1}{2}} - 1)$ and also
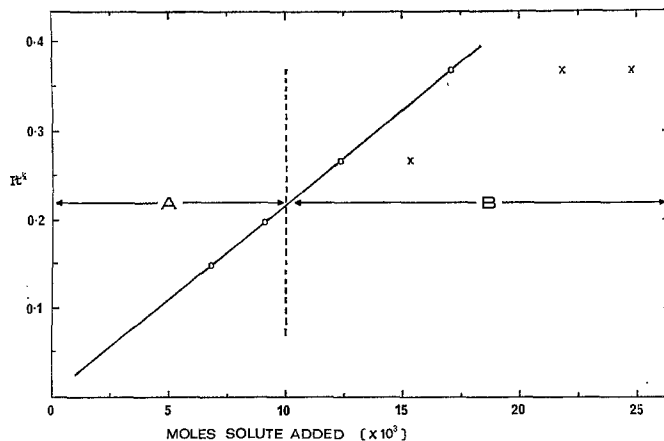

Fig. 7. Variation of $I\tau^{\frac{1}{2}}$ with moles solute added to approximately 100 cm^3 LiCl–KCl eutectic (○) = moles Pb^{2+} added (×) = moles Pb^{2+} + moles SO_4^{2-} added. Temperature = 410°C. (Note: Region A no sulphate present in melt. Region B contains sulphate and lead ions.)

versus log $(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})$. It was found that the latter equation gave the best linear plot. A typical plot is shown in Fig. 6. The slope of the linear curves were similar, being 67 mV which is equivalent to $RT/2F$. This is also identical with the shape found by Inman and Bockris [18] for PbCl₂ in LiCl–KCl eutectic and indicative that the cathode reaction is

$$Pb^{2+}_{(molten\ salt)} + 2e \rightleftharpoons Pb_{(liquid)} \qquad (10)$$
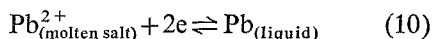
although it does not conclusively disprove the electro-reduction of the sulphate anion.

Since Inman and Bockris have shown that the electro-reduction of lead ions obeys Sands equation, a test to confirm that the sulphate anion is not directly electro-reduced can be made by examining the relationship between $i\tau^{\frac{1}{2}}$ and moles of solute added. This was carried out by making successive additions of PbCl₂ to the solvent followed by two additions of PbSO₄ and finally an addition of anhydrous K₂SO₄. Results are presented in Fig. 7 and they show the expected correlation only with lead ions. Clearly, the presence of sulphate anions has no influence on the transition times. Furthermore no new chronopotentiometric wave was introduced either at potentials below or above that for lead ion reduction.

The diffusion coefficient of the lead ions, as calculated from the curve in Fig. 7 and the electrode geometry was $3 \cdot 0 \times 10^{-5}$ cm²s⁻¹ at 410°C. Since only the geometric area of the graphite rod was used in this calculation, the value compares favourably with the published value of approximately $3 \cdot 0 \times 10^{-5}$ cm²s⁻¹ at 400°C [18].

4. General discussion

The observed decrease in current efficiencies appears to be due to a reaction between lead sulphate and the electrodeposited lead. The rate of this reaction is dependent on the concentration of lead sulphate rather than the sulphate anion. This may be due to lead sulphate influencing the rate of dissolution of the oxide film formed by the initial reaction between the lead metal and the sulphate anion. The formation of the melt-soluble basic lead sulphate in this way would imply that the reaction is strongly favoured thermodynamically.

Since the chronopotentiometry indicates that the sulphate anion does not introduce complications in the cathode process. there should be a good correlation between the current efficiency losses and those expected from the rate of loss of lead.

Assuming the lead losses to be independent of current then the efficiency decrease would be given by the following expression:

$$\text{Efficiency decrease (\%)} = \frac{100\ R.A.}{i.F.} \qquad (11)$$

where R is the rate of loss of lead (i.e., Section 3·2) in g. atoms cm⁻² s⁻¹, A the total area of lead, i the applied current and F Faraday's constant.

The only system in which these two measurements (i.e., efficiency decrease and lead loss) were made under identical conditions was a melt containing 4·4 mole % PbSO₄ in LiCl–KCl eutectic at 430°C. For this system, the initial rate of oxidation of lead is $9 \cdot 3 \times 10^{-6}$ g. atoms cm⁻² s⁻¹, while we have calculated that the average area of lead exposed to the melt was $1 \cdot 7 \pm 0 \cdot 3$ times the geometric area of the electrode. The latter figure takes into account the area of both the metal pool and the working electrode.

Using these values, we obtain the expected decreases given in Table 1 where they are compared with decreases read off the curve A of Fig. 1.

Table 1. *Calculated and observed efficiency losses at* 430°C

Melt 4·4 mole % PbSO₄ in LiCl–KCl eutectic

Current Density A cm⁻²	0·02	0·05	0·1	0·2	0·3
Calculated % loss	7·8	3·2	1·7	0·7	0·5
Observed % loss	8·9	6·5	2·8	0·7	0·4

The agreement between the two sets of data is close and within the limits of accuracy of the data except for the values at 0·05 A cm⁻². However in that case the discrepancy is not much greater than the limits of experimental error, as is evident by the scatter of points defining curve A of Fig. 1. Similar agreement can be found with

other efficiency data when using rate constant estimated from the trends found in this investigation. We consider this correlation to be added support that the deposition of lead proceeds according to Equation 10 and the loss in efficiency is due to a reoxidation process as given by Equation 9, the rate of which is independent of electrode potential.

Acknowledgement

References

[1] G. C. Bratt and R. W. Pickering, *Met. Trans.*, **1** (1970) 2141.

[2] C. H. Liu, *J. Phys. Chem.*, **66** (1962) 164.

[3] K. E. Johnson and H. A. Laitinen, *J. Electrochem. Soc.*, **110** (1963) 314.

[4] D. M. Wrench and D. Inman, *Electrochem. Acta*, **12** (1967) 1601.

[5] S. Senderoff, E. M. Klopp and M. L. Kronenberg. Eighth and Ninth Quarterly Technical Prog. Reports Contract NORD 18240 (1960).

[6] B. Woodall quoted by H. Laitinen, *Talanta*, **12** (1965) 1237.

[7] B. W. Burrows and G. J. Hills, *Electrochim. Acta*, **15** (1970) 445.

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

[9] F. I. L'vovich, S. A. Zaretskii and A. G. Morachevskii, *Zhur. Phys. Khim.*, **40** (1967) 828.

[10] A. A. Roudnitzki and I. P. Tverdovsky, *Zhur. Phys. Khim.*, **9** (1936) 26.

[11] P. L. King and B. J. Welch. Submitted for publication. P. L. King Ph.D. thesis, University of New South Wales, 1971.

[12] B. J. Welch, P. L. King and R. A. Jenkins, *Scand. J. Metallurgy*, **1** (1972) 49.

[13] A. G. Bergman, Yu. J. Andryischenko and R. K. Bineeva, *J. Inorg. Chem., U.S.S.R.*, **8** (1963) 880.

[14] H. H. Kellogg, *Trans. Met. Soc. A.I.M.E.*, **230** (1964) 1622.

[15] W. H. Reinmuth, *Anal. Chem.*, **33** (1961) 322.

[16] M. Paunovic, *J. Electroanal. Chem.*, **14** (1967) 447.

[17] D. Inman, R. S. Sethi and R. Spencer, *J. Electroanal. Chem.*, **29** (1971) 137.

[18] D. Inman and J. O'M. Bockris, *J. Electroanal. Chem.*, **3** (1962) 126.