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# Electrochemical reduction of lead chloride on some solid electrodes in fused NaCl–KCl mixtures

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The electrochemical reduction of $PbCl_2$ has been studied in a fused NaCl–KCl mixture with tungsten, molybdenum and nickel electrodes. Experiments were conducted in the 700–850° C temperature range using voltammetric and chronopotentiometric techniques. Poor lead adhesion to the electrode surface made the study with the nickel electrode impossible and the results obtained with the tungsten electrode somewhat doubtful. Lead adhesion to the molybdenum surface was good but the experimental curves had to be corrected for a cathodic residual current. The lead chloride reduction appears to occur reversibly according to the reaction

$$PbCl_2 + 2e^- \longrightarrow Pb + 2Cl^-$$

No evidence of lead metal solubility in the melt was found. The lead ion diffusion coefficient obeys the Arrhenius Law:

$$D_{Pb(II)} = 10^{-3} \exp(-2957/T) \, cm^2 \, s^{-1}$$

in the temperature range 700 to 850° C.

## 1. Introduction

Lead has been extensively used in the manufacture of batteries. Its common hydro or pyrometallurgical winning and refining processes [1] consume a great deal of energy and cause pollution. Moreover, they may not be well suited to the recovery of the antimony, copper or silver contained in the ore. This explains why recent research has focused on lead electro-winning and electro-refining [2–8] as alternative processes.

A recent review [9] has shown the value of lead chloride electrolysis in fused alkali chloride mixtures since it gives liquid metal. Due to the high reactivity of LiCl with moisture NaCl-KCl-$PbCl_2$ mixtures have been chosen for the electrolyte and their electrochemical properties have been studied. Previous studies [10–12] of the equilibrium between lead and such solutions have given evidence of $PbCl_n^{2-n}$ complexes and the apparent standard potential value, $E'_{ox}$Pb(II)/Pb, has been well established.

Many kinetic experiments on lead chloride reduction in fused LiCl–KCl–$PbCl_2$ mixtures and similar chloride melts have been reported in the literature [13–20]. Most of the early experiments propose diffusion control for the reduction process, but there is a discrepancy between the values obtained for the lead ion diffusion coefficient. Moreover, Delimarskii *et al.* [18], and more recently Stenberg *et al.* [20], have concluded that Pb(II) ion reduction occurs involving the formation of monovalent lead ions. Finally, Piron [19] has observed anodic and cathodic passivation of molten lead. Little information has been given on the influence of temperature, the interaction between lead and substrates and on lead solubility in the melt.

In order to examine these details, this study was conducted using chronopotentiometric and voltammetric techniques with tungsten, molybdenum and nickel electrodes in the 700–850°C temperature range.

## 2. Experimental details

The experimental device employed here has been described previously [21]. The solvent was contained in a quartz vessel. Water and oxygen were removed from the melt by heating it in a vacuum and fusing it in a dry argon atmosphere. Metallic impurities, less electronegative than lead, were removed by adding some lead metal. Lead chloride was introduced in an argon flow through a locked chamber. The working electrode consisted of a wire 1 mm in diameter, the area of which was limited by the immersed part. The potentials were referred to the Ag/AgCl in NaCl–KCl half cell built with a thin Pyrex junction. The current-time or potential-time transients were applied using an EEG PAR 173 potentiostat-galvanostat controlled by

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an EEG PAR 175 pulse generator. The experimental data were recorded using a digital storage oscilloscope Nicollet 2090 A for further processing.

## 3. Electrochemical reduction of lead chloride

The experiments were carried out over a chloride concentration range of $5 \times 10^{-3}$ to $10^{-1}$ M. The temperature was usually 700°C but some experimental results were obtained in the 700–850°C range.

### 3.1. *Results for a tungsten electrode*

*3.1.1. Poor lead adhesion.* A lead electrode can be prepared *in situ* by reducing the lead chloride to the metal on the tungsten surface, but the lead adhesion must be good. Adhesion was studied by chronopotentiometric experiments.

From the chronopotentiograms with current reversal, it was noticed that the anodic transition time was shorter than the cathodic transition time. Part of the lead metal corresponding to the reduction escaped from the electrode surface during the polarization, *i.e.* poor lead adhesion to the tungsten electrode surface occurred. Meaningful kinetic studies therefore require fast sweep rates for voltammetry and high current densities for chronopotentiometry. In any case, the results of the lead chloride reduction study on a tungsten electrode have to be with other electrode materials.

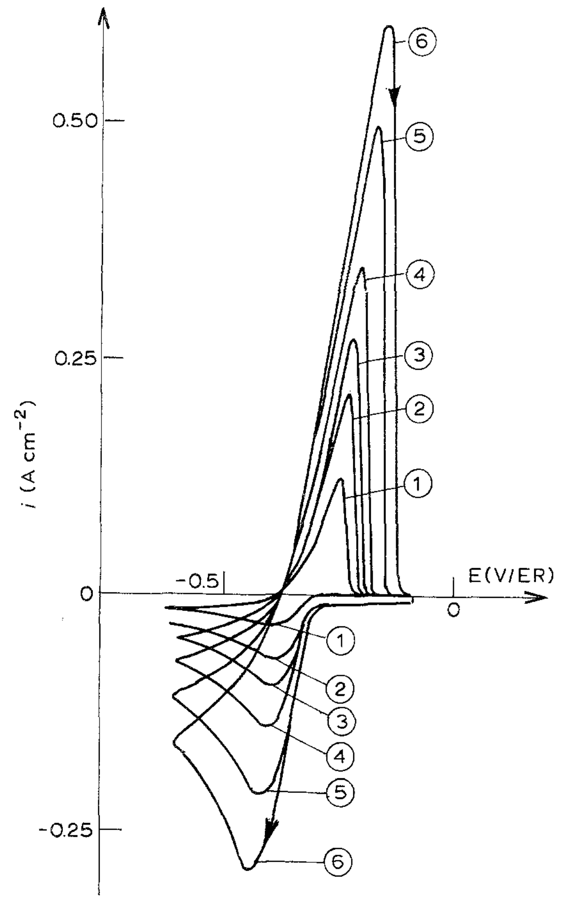

Fig. 1. Voltammetric study of lead chloride reduction. Temperature: 700° C; $PbCl_2$ concentration: 0.017 M; working electrode: tungsten; sweep rates: (1) 0.4, (2) 1.6, (3) 3.2, (4) 6.4, (5) 12.8 and (6) 25.6 V s$^{-1}$.

*3.1.2. Reversibility of lead chloride reduction on a tungsten electrode.* The reversibility of lead chloride reduction was studied using both voltammetric and chronopotentiometric techniques.

*Voltammetric analysis.* Figure 1 presents a number of voltammograms for the reduction of lead chloride on a tungsten electrode. On each curve one cathodic peak ($E_p \simeq -0.4$ V/ER) and, on the anodic part of the curve, one sharp anodic stripping peak are seen. The shape of the voltammograms, and especially the break corresponding to the beginning of lead chloride reduction, is characteristic of the formation and the reoxidation of a product of constant activity; it gives no evidence for lead solubility.

Due to the high current flowing through the electrode, the voltammetric transients are affected by the ohmic drop interferences and, consequently, must be analysed using a convolution procedure [22, 23]; (*cf.* Appendix 1). The semi-integral of the current $m(t) = (1/\pi)^{-1/2}\int_0^t i(u)(t-u)^{-1/2}\,\mathrm{d}u$ was computed.

A series of convoluted curves, $m = f(E)$, related to the voltammograms of Fig. 1 are represented in Fig. 2 after correction for the ohmic drop. We verified that the different curves were similar and that the direct and reverse scans were the same for each curve. This proves the reversibility of the lead chloride reduction.

The logarithmic analysis of a convoluted curve corresponding to a sweep rate of 0.1 V s$^{-1}$ is given in Fig. 2. The electrode potential varies linearly with $\ln(1 - m/m^*)$ with $m^* = nFC_0\sqrt{D_{ox}}$. the slope of the linear part of this curve yields the number of electrons exchanged, $n \simeq 2.04$. The results are in accordance with lead insolubility in the fused NaCl–KCl–$PbCl_2$ mixture and show the reversibility of the reduction reaction.

*Chronopotentiometric analysis.* Figure 3 presents a number of chronopotentiometric transients obtained on a tungsten electrode. The shape of the curves is characteristic of a soluble/insoluble process.

If the transition time is not too long, i.e. shorter than 0.5 to 1 s, Sand's relation is obeyed. Under these conditions the logarithmic analysis of chronopotentiograms is possible. One example is given in Fig. 4. The electrode potential varies linearly with $\ln[1 - (t/\tau)^{1/2}]$. The slope of the linear part of the curve, 0.038 V, approaches the theoretical value, 0.043 V, for a two electron reversible exchange process at 700°C. Thus the experimental results are in accordance with the insolubility of lead and the reversibility of the Pb(II)/Pb exchange process.

### 3.2. *Results obtained using nickel and molybdenum electrodes*

*3.2.1. Non-adhesion of lead to the nickel electrode.* On the voltammograms obtained at a nickel electrode it is

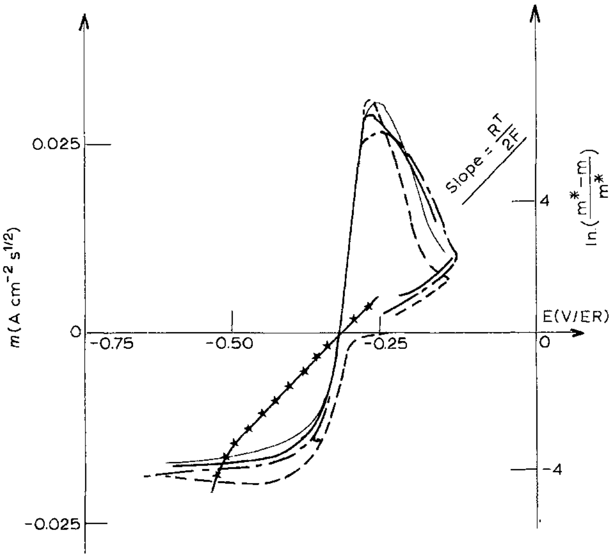

Fig. 2. Semi-integral curves of voltammograms on Fig. 1 (———) and their logarithmic analysis (* * *).

seen that some oscillations occur in the current; these are probably due to the convection resulting from the fall of liquid metal drops. The nickel electrode therefore cannot be used for the kinetic study.

*3.2.2. Reversibility of lead chloride reduction on the molybdenum electrode.* A number of voltammograms corresponding to the reduction of lead chloride on a molybdenum electrode are shown in Fig. 5.

As with a tungsten electrode the shape of the curves is again characteristic of the formation of an insoluble species. For all the sweep rates chosen, lead metal shows good adhesion to the electrode surface. Unfortunately, a residual cathodic current appears before the lead chloride reduction and therefore the transients cannot be directly analysed using a convolution procedure.

It was noticed that the residual current also exists for the pure solvent. It was assumed that the reversibility of the reaction could be studied using the curves corrected for the residual current.

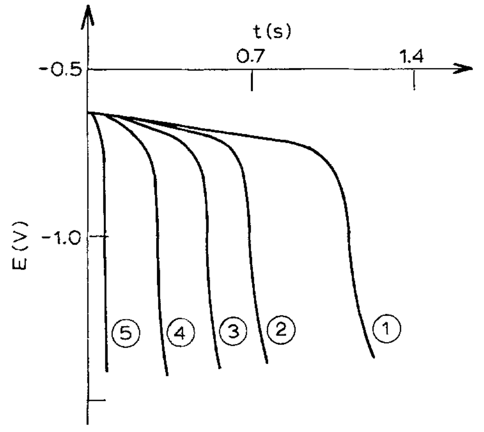

Fig. 3. Chronopotentiometric study of lead chloride reduction. Temperature: 700° C; $PbCl_2$ concentration: 0.018 M; working electrode: tungsten; cathodic current density $|i_c|$: (1) 0.020, (2) 0.026, (3) 0.030, (4) 0.040 and (5) 0.070 A cm$^{-2}$.

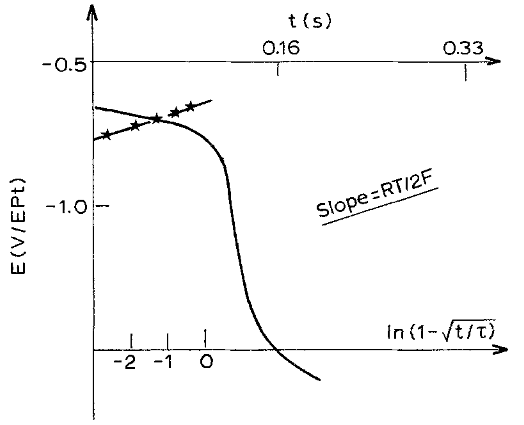

Fig. 4. Chronopotentiometric transient (———) and its logarithmic analysis (* * *). Temperature: 700° C; $PbCl_2$ concentration: 0.018 M; and cathodic current density $|i_c| = 0.05$ A cm$^{-2}$.

Fig. 6 shows a corrected voltammogram. The convoluted curves of the corrected voltammograms remain the same when the sweep rate varies. This is characteristic of a reversible process.

## 4. Study of lead ion diffusion

The kinetic study with the tungsten and molybdenum electrodes suggests that lead chloride reduction occurs reversibly and that lead is insoluble in the melt. The lead ion diffusion coefficient can be computed from voltammetric and chronopotentiometric data and the boundary semi-integral values according to the following relations:

$$i_p = 6.35 \times 10^{-6}\, C_0 D_{ox}^{1/2} v^{1/2} R^{-1/2} T^{-1/2}$$

$$m^* = nFC_0 D_{ox}^{1/2}$$

$$i\sqrt{\tau} = nFC_0 \pi^{1/2} (D_{ox}/2)^{1/2}$$

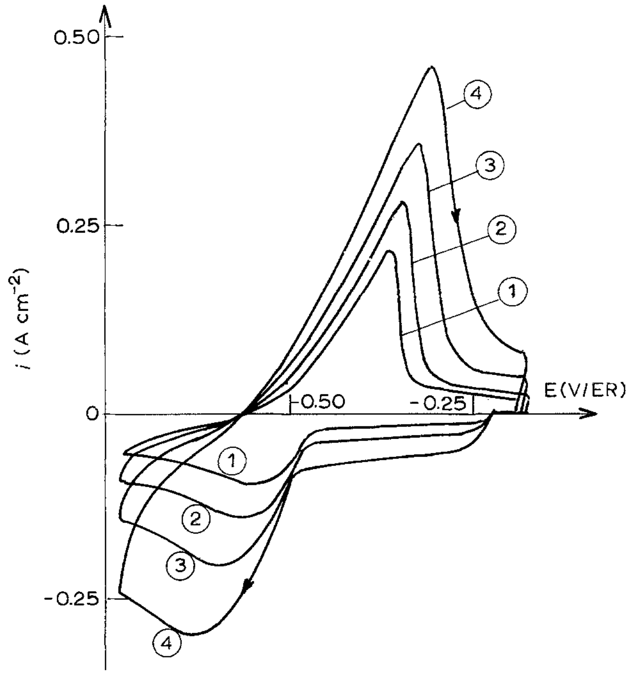

Fig. 5. Voltammetric study of lead chloride reduction on the molybdenum electrode. Temperature: 700° C; $PbCl_2$ concentration: 0.017 M; sweep rates: (1) 1.6, (2) 3.2, (3) 6.4 and (4) 12.8 V s$^{-1}$.

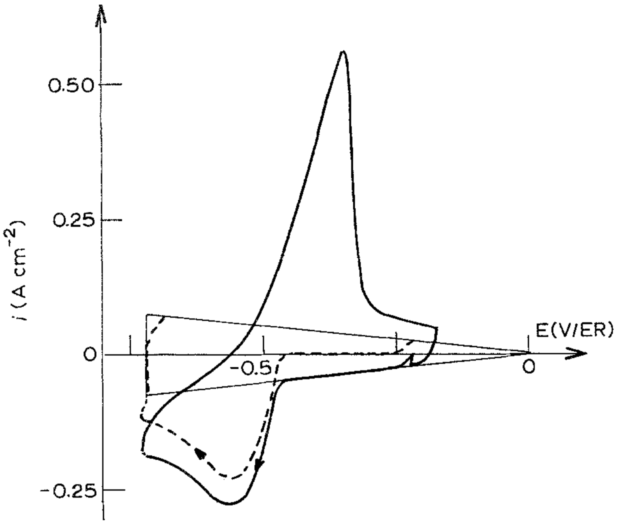

Fig. 6. Voltammetric study of lead chloride reduction: principle of correction for the residual current. Temperature: 700° C; $PbCl_2$ concentration: 0.01 M; sweep rate: 3.2 V $s^{-1}$.

where $i_p$ is the peak current density, $C_0$ the bulk concentration of the oxidized species, $D_{ox}$ the diffusion coefficient of the oxidized species, $v$ the sweep rate, and $\tau$, the transition time.

At 700° C, using these relations, the results are:

$D_{Pb}(II) = 4.0 \times 10^{-5}\,cm^2\,s^{-1}$ curve $i_p = f(v)^{1/2}$, Fig. 7

$D_{Pb}(II) = 4.4 \times 10^{-5}\,cm^2\,s^{-1}$ $m^*$ value, Fig. 2

$D_{Pb}(II) = 4.0 \times 10^{-5}\,cm^2\,s^{-1}$ $i(\tau)^{1/2}$ value, §3.1.2.

The curves $i(\tau)^{1/2}$ against $i$ shown in Fig. 8 have been obtained for different temperatures, from 700 to 850° C. Sand's relation holds, as earlier, for the lower transition times ($\tau < 1$ s). The lead ion diffusion coefficients computed from these data are reported in Table 1.

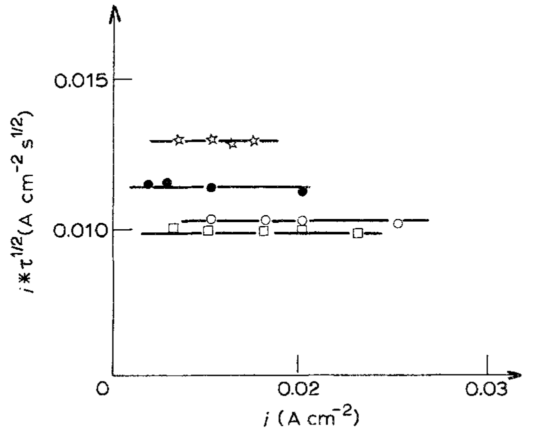

Fig. 8. Study of lead ion diffusion. Curve $i(\tau)^{1/2} = f(i)$. (□) 710, (○) 750, (●) 800 and (☆) 850° C. $PbCl_2$ concentration: 0.084 M.

*Table 1. Lead ion diffusion coefficients at different temperatures*

| θ°C | 710 | 750 | 800 | 850 |
|---|---|---|---|---|
| $10^5\,D_{Pb(II)}$ ($cm^2\,s^{-1}$) | 4.7 | 4.9 | 5.5 | 6.2 |

From the linear variation in ln $D$ with $T^{-1}$ (Fig. 9), both the activation energy of the diffusion process and the pre-exponential term were obtained. These are, respectively, $E_A \simeq 24600\,J\,mol^{-1}$ and $D_{Pb(II)} = 10^{-3}\exp(-2957/T)\,cm^2\,s^{-1}$.

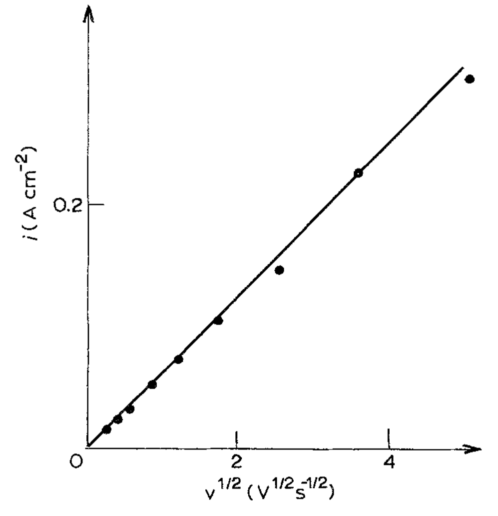

Fig. 7. Study of lead ion diffusion. Curve $i_p = f(u)^{1/2}$. Temperature: 700° C; $PbCl_2$ concentration: 0.017 M.

## 5. Conclusion

The study of the reduction of $PbCl_2$ at various solid electrodes gives some information about the reduction of Pb(II) species and the interaction of lead with the substrate surface.

Using voltammetric and chronopotentiometric techniques, it was observed that the reduction of lead chloride at the tungsten electrode occurs reversibly but the adhesion of liquid lead at the surface is poor. The metal leaves the electrode surface during the polarization phase. Evidence of the insolubility of lead in the fused electrolyte was found in all cases.

From the studies on molybdenum electrodes, however, for which the experimental curves had to be

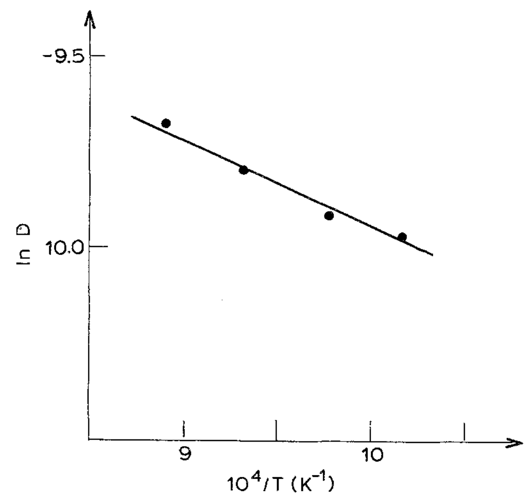

Fig. 9. Study of lead ion diffusion. Curve ln $D = f(1/T)$.

corrected for the residual current occurring in the pure solvent, the conclusions were the same as above.

When lead adhesion at the electrode surface was good, and when Sand's relationship held, the diffusion coefficient of Pb(II) ions and the corresponding activation energy could be calculated.

The present results support diffusion control for lead chloride reduction. The experimental curves reported recently by Stenberg *et al.* [20] for lead reduction in fused $LiCl$-$KCl$-$PbCl_2$ mixtures may be due to convection resulting from the use of a molten lead electrode and not to the reactions between lead and lead chloride.

At 700° C, our value for the Pb(II) diffusion coefficient is consistent with those obtained from impedance measurements by Ukshe *et al.* [16].

For the diffusion process, the activation energy computed is higher than the value obtained by Stein [13].

## Appendix 1
## Convolution procedure [21–22] (Soluble/insoluble reversible exchange

In the case of semi-infinite linear diffusion, Fick's law solutions are expressed versus the current semi-integral. For the reduction of a soluble species we get:

$$C(0,\, t) \;=\; c_0 + m(t)/nF\sqrt{D_{\mathrm{ox}}}$$

in which $C(0, t)$ is the concentration of oxidized species on the surface electrode at time $t$, $C_0$, is the bulk concentration of oxidized species, $m(t)$, is $1/\sqrt{(\pi)}\int_0^t i(u)\,(t-u)^{-1/2}\,\mathrm{d}u$, and $m(t) \to m^*$ when $C(0, t) \to 0$.

Then, for a reversible soluble/insoluble process, according to the Nernst equation

$$E \;=\; E_{\mathrm{th}} + (RT/nF)\ \ln\,[(m^* - m(t))/m^*]$$

in which $E_{\mathrm{th}} = E^0 + (RT/nF)\ln C_0$.

Here the electrode potential only depends on the semi-integral.

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