

## DEPOSITION OF ZINC ON MOLTEN LEAD BY ELECTROCHEMICAL TECHNIQUES IN MOLTEN LiCl-KCl

M KAMALUDEEN, K BALAKRISHNAN,

Central Electrochemical Research Institute, Karaikudi 623 006, INDIA

GURDEEP SINGH and N S RAWAT

Indian School of Mines, Dhanbad, INDIA

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The electrochemical incorporation of Zn onto molten Pb working electrode from molten eutectic of LiCl and KCl containing 0.0179, 0.0313 and 0.0477 mol ZnCl<sub>2</sub> at 673K was investigated by cyclic voltammetry at different scanning rates and by chronocoulometry. The results show that the initial formation of lead-zinc solid solution is followed by the formation of Pb-Zn intermetallic compound.

**Key words:** Molten cathodes, alloy formation, chronocoulometry

### INTRODUCTION

Several authors [1-4] have investigated the incorporation of various elements, especially Li metal, into molten Al by cyclic voltammetry [2], chronocoulometry, potentiostatic and galvanostatic techniques [3,4]. Alloy formation with Mg [5,6], Sb, Bi, Se, Te, Pb and other liquid cathodes has also been widely studied [7-20].

The present investigation is on the mechanism of some of the binary and ternary alloys of Pb formed during fused salt deposition on molten lead. The systems such as Pb-Zn, Pb-Sn and Pb-Sn-Zn have been examined, both from the point of view of mechanism and corrosion resistance.

### EXPERIMENTAL

#### Preparation of melts

Stringent measures are normally taken in preparing melts in anhydrous condition. This becomes essential to avoid the deleterious effects of moisture. The presence of moisture not only results in hydrolytic decomposition, but also attacks the container, and the electrode materials, as well as degrade the quality of the product and diminish the usable potential range of the solvent. Simple heating may not be effective in removing all the water molecules. Special procedures have to be followed in making them suitable for basic studies.

For eutectics like LiCl + KCl and NaCl + ZnCl<sub>2</sub> mainly two procedures have been followed [21,22]. The first method depends on the prolonged heating of the mixture under dry HCl followed by bubbling dry argon to remove the excess HCl. The second method consists of bubbling pure dry chlorine gas for about one hour through the melt immediately after fusion of the undried salt mixture. Any residual chlorine could be removed by bubbling dry argon through the melt for about 20 minutes. Both the methods are considered to be efficient in removing moisture from melts; nevertheless the latter one seems to be convenient as it is less time consuming compared with the prolonged bubbling of dry HCl. Besides the above operation, prolonged electrolysis [23] of the melt

between carbon electrodes has added advantage in removing the electroactive impurities including moisture.

An all-glass cell set up has been used. The experimental cell consisted of a glass cell of 4 cm dia and 10 cm height protected by an outer glass jacket of 6 cm dia, being externally heated by a resistor furnace operating at temperature up to 773K with controller. Provision was made for introducing the anode, cathode, reference electrode, thermocouple, vacuum tube and chlorine/argon gas tube as and when required with suitable ground seatings during the course of the experiment.

A silver/silver chloride reference electrode with eutectic mixture LiCl and KCl containing 0.1 m/o silver chloride [24] was used. The lower capillary tip was plugged with asbestos [25,26] in order to prevent the mixing of the eutectic with the remaining electrolyte and at the same time maintaining electrical contact.

An intimate mixture of AR lithium and potassium chlorides corresponding to the eutectic composition (58.5 : 41.5 m/o) was taken in a glass stoppered conical flask. After thorough mixing, the contents were transferred into the 4 cm dia glass cell and placed inside the glass heating jacket. The following procedure was followed in preparing anhydrous eutectic suitable for electrochemical study.

The cell was first evacuated and pure dry argon was passed through to maintain a pressure of 1 atmosphere. The temperature was slowly raised to 473K with argon flowing through the powdered mixture. Argon was replaced by dry chlorine and the mixture was melted by raising the temperature to 673K. After bubbling chlorine through the molten eutectic for 1 hour, it was replaced by argon for 20 minutes in order to remove excess occluded chlorine. The rest of the experiment was carried out under the blanket of argon. The melt was then electrolysed overnight at 1.6 V between two graphite electrodes until the residual current became low. The temperature of the melt was maintained at 673K + 5K as measured by a glass sheathed chromel-alumel thermocouple in contact with the melt.

The removal of last traces of moisture from the molten eutectic was confirmed by the polarographic study employing platinum

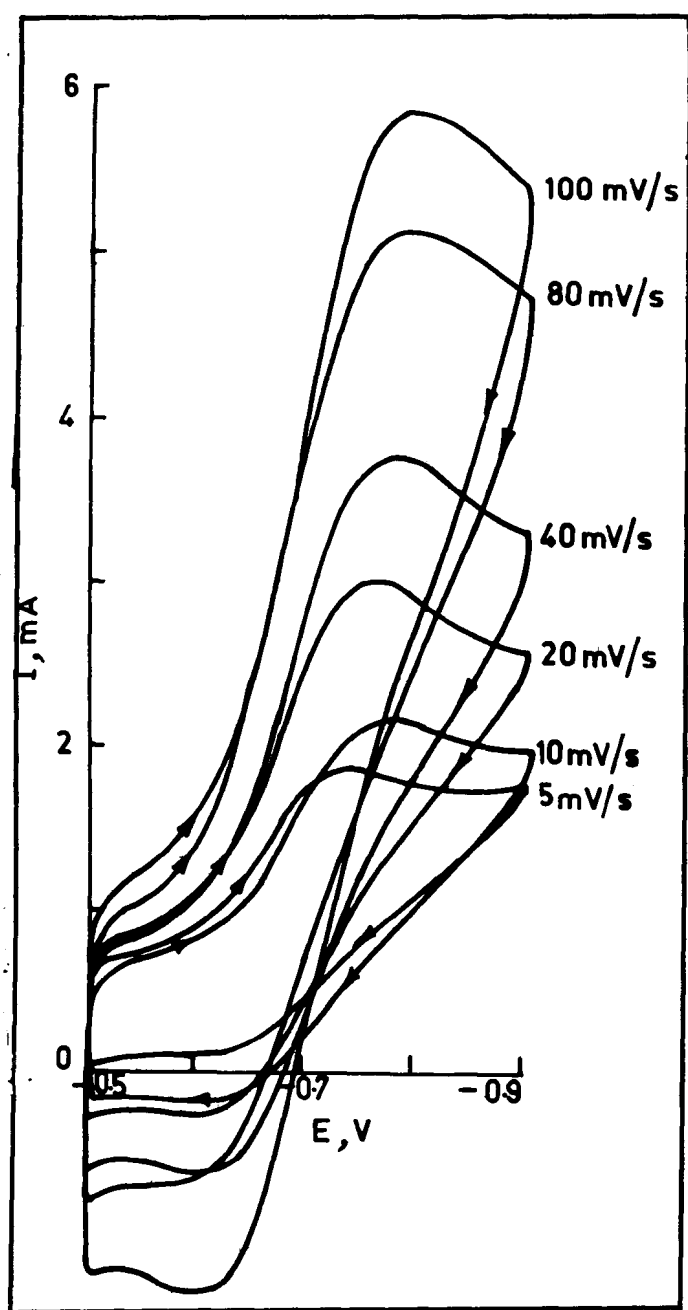


Fig. 1: Voltammogram of molten lead electrode ( $A = 0.283 \text{ cm}^2$ ) in lithium chloride + potassium chloride eutectic containing 0.0179 m/kg zinc chloride at 673K from -0.500 - 0.900V wrt Ag/AgCl

microelectrode (area:  $0.0157 \text{ cm}^2$ ) and tungsten counter electrode with respect to Ag/AgCl reference electrode. The potential of the working electrode was subjected to linear scanning from 0 to -1.8V at sweep rate of 5 mV/sec. The absence of electroactive impurities including moisture was indicated by the negligible residual current.

After taking out the microelectrodes from the purified melt, a glass tube holder of 6 mm internal dia with a U bend of 20 mm height at the lower end was introduced with pieces of spec pure lead. The lead got melted as soon as the holder was immersed into the melt. Electrical contact to the molten lead was provided by a tungsten wire tip fused to a glass tube. By this arrangement working electrode area of  $0.283 \text{ cm}^2$  was made available for the experiment. The proper seating of the glass holder at the top lid was made possible by the B24 ground joint. The counter electrode was 5 mm dia spec pure graphite rod suspended from the top. The depth of immersion of the rod in the melt could be adjusted by the top threading arrangement. A syringe feeding arrangement attached to the glass cell was used for adding the solute without moisture intake.

A Wenking Potentiostat was employed for recording the voltammogram in the experiments. Scan rates were varied from 5 to 100  $\text{mV}/\text{sec}^{-1}$ .

### RESULTS AND DISCUSSION

The typical voltammograms of Zn deposition on molten Pb from LiCl + KCl melt at 673K containing zinc chloride at the concentration of 0.0179 m/kg of the melt, recorded for different sweep rates, are given in Fig. 1.

The general features of the voltammograms recorded for other concentrations and sweep rates were similar to those given in Fig. 1. As the rest potential of the molten lead working electrode was found to be -0.480 V wrt Ag/AgCl reference electrode the potential range of the working electrode was scanned from -0.500 to -0.900 V. In order to expose fresh surface while taking voltammogram the working electrode i.e. spec pure lead, was changed for each concentration of  $\text{ZnCl}_2$ , but the electrode itself was stirred with tungsten wire before the study at different sweep rates at a particular concentration.

The  $E_{P/2}$  values and cathodic peak current  $i_p^c$  for each concentration at various sweep rates are given in Table 1.

From Table I it is observed that there is a steady increase in the

TABLE-I: Secondary data from cyclic voltammograms (Fig.1)

Concn. of zinc chloride m/kg	Sweep rate mV/sec.	$i_p^c$ mA	$E_{P/2}$ V	$i_p^A$ mA
0.0179	5	1.83	-0.660	--
	20	2.97	-0.675	0.26
	40	3.69	-0.685	0.59
	80	5.04	-0.685	0.69
	100	5.77	-0.690	1.35
0.0313	10	4.40	-0.685	0.60
	20	5.55	-0.695	1.20
0.0477	10	7.50	-0.690	2.00
	20	7.80	-0.690	2.20
	40	10.40	-0.695	3.40

cathodic peak current with sweep rate and zinc chloride concentration and very little change in the  $E_{P/2}$  values. The plot of  $i_p^c$  vs  $v^{1/2}$  shows the linear relationship (Fig. 2). It indicates that it is a diffusion controlled process.

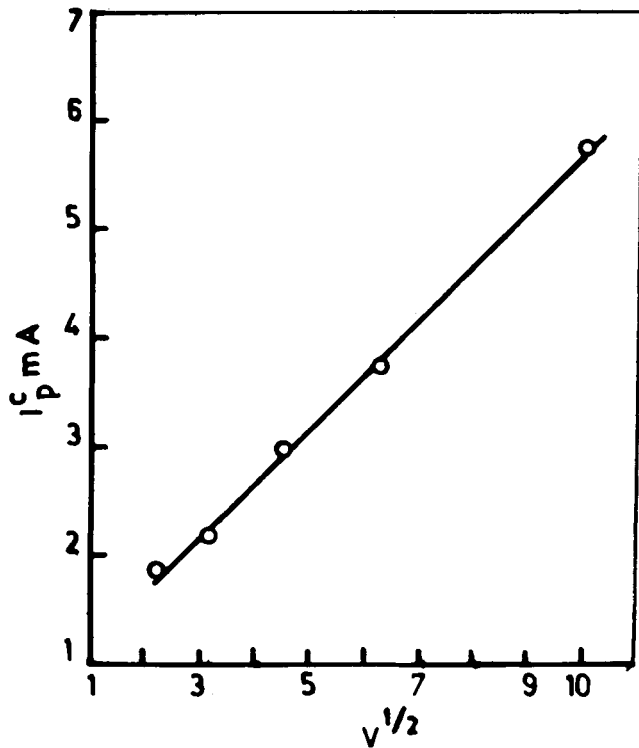


Fig. 2: Plot of  $i_p^c$  vs square root of sweep rate at  $ZnCl_2$  concentration 0.0179 m/kg

### Chronocoulometry

Chronocoulometric measurements were made at  $673 \pm 5K$  in the same set-up to determine the mechanism of alloy formation during the deposition of zinc on molten lead working electrode.

A potentiostat/galvanostat PAR Model 173 was used for the constant potential mode. Current integration was conveniently accomplished by using digital coulometer. The potential of the working electrode was stepped up from its rest potential of  $-0.500$  V to the desired more negative value of  $-0.608$ ,  $-0.656$ ,  $-0.703$  and  $-0.785$  V and the coulombs passed during the controlled potential electrolysis for 5, 10, 15, 20 seconds were recorded independently from the digital coulometer. The values are given in Table II

Fig. 3 shows the plot of coulombs vs applied potential for the reduction of  $Zn^{2+}$  from LiCl + KCl eutectic containing 0.0477 m/kg  $ZnCl_2$  at 673K on molten Pb electrode. If the incorporation rate of the discharging ion is limited by the diffusion mechanism, the total charge  $Q$  passed will be proportional to the square root of time ( $\sqrt{t}$ ) and when the rate is limited by a reaction to form inter-

TABLE-II: Data from chronocoulometric analysis at different potentials

Stepped up potential, mV	Coulombs recorded in			
	5 Sec.	10 Sec.	15 Sec.	20 Sec.
-608	15.2	21.7	28.6	34.2
-656	14.9	24.2	31.6	40.3
-703	15.2	23.9	38.4	53.3
-785	44.1	79.0	83.6	96.5
-850	115.9	228.3	284.1	385.8

metallic compound,  $Q$  is proportional to  $t$  [1, 4]. Plots of total charge passed vs square root of time for the various stepped up potentials are shown in Fig. 4. The linearity of the curve up to potential  $-656$  mV indicates that the incorporation of zinc on molten lead is diffusion-controlled at the initial stages.

The departure from linearity at potentials more than  $-656$  mV indicates that the incorporation is no longer diffusion controlled

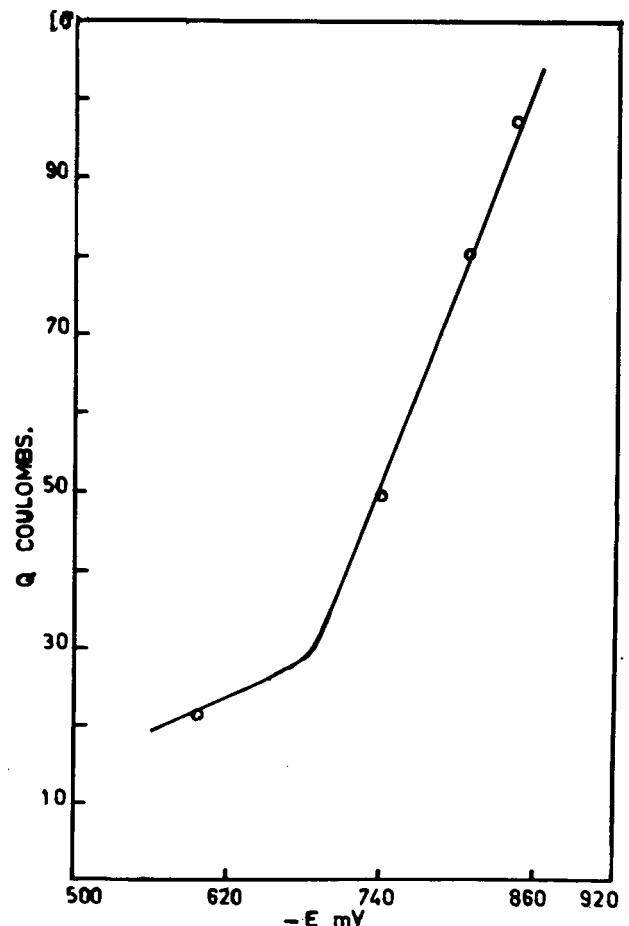


Fig. 3: Plot of coulombs vs applied potential for the reduction of  $Zn^{2+}$  from LiCl + KCl eutectic containing 0.0477 m/kg  $ZnCl_2$  at 673K on molten Pb cathode  $A = 0.283$  cm<sup>2</sup>.

Plots are drawn showing the relation between Q vs t for the higher stepped up potentials as shown in Fig.5.

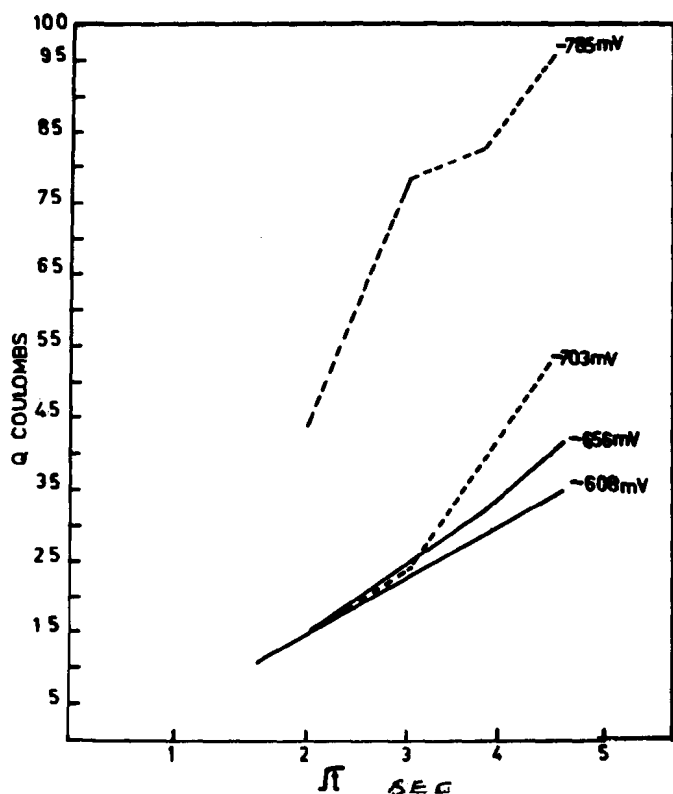


Fig. 4: Plot of coulombs vs square root of time for the reduction of  $Zn^{2+}$  from LiCl + KCl eutectic containing 0.0477 m/kg  $ZnCl_2$  at 673K on molten Pb cathode

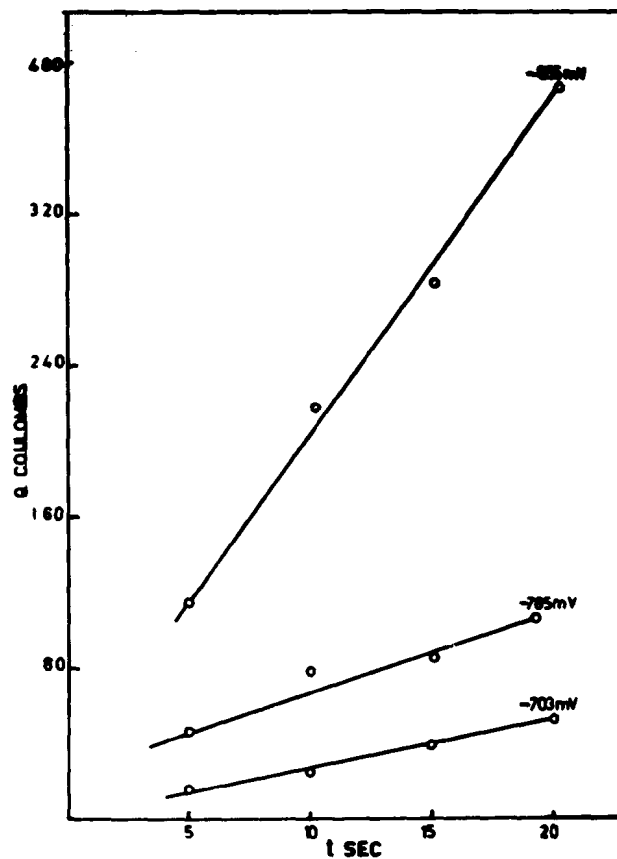


Fig. 5: Plot of coulombs vs time for the reduction of  $Zn^{2+}$  from LiCl + KCl eutectic containing 0.0477 m/kg  $ZnCl_2$  at 673K on molten Pb cathode

Linearity of the graph may be the result of intermetallic compound formation between zinc and lead at these overpotentials. Evidently, the observation of alloy formation is in accordance with the phase diagram [27] of Pb and Zn which shows that after the initial eutectic formation of Pb and Zn with 0.5 m/o Zn at 591K the formation of intermetallic compounds occurs with the increase in Zn content.

Hence in the electrodeposition of zinc on molten lead electrode, the rate of incorporation appears to be governed initially by diffusion-controlled mechanism and after the formation of solid solution a transition to intermetallic compound formation occurs.

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