

## Short Communication

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# Electrochemical studies on a zinc-lead-cadmium alloy in aqueous ammonium chloride solution

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### Abstract

Studies are reported of the anodic polarization behaviour of a zinc-lead-cadmium alloy in aqueous ammonium chloride solution over a wide range of current densities between 5 and 1000 mA cm<sup>-2</sup>. A casting method is employed to prepare the electrode; the alloying constituents are analysed by atomic absorption spectroscopy (AAS). It is found that both the internal resistance and the anodic potential of the systems are at a minimum in 5.5 N NH<sub>4</sub>Cl. The data has been compared with those obtained for pure zinc and it is concluded that the present alloy is a better electrode throughout the polarization range of this investigation. A conventional weight-loss method shows that the corrosion rate is greater than that exhibited by pure zinc. Scanning electron micrographs of the post-immersed surface are compared with those for the pre-immersed surface. Supplementary investigations of linear polarization have been conducted in order to gain an understanding of the system for a narrow perturbation range of potential.

### Introduction

In Leclanché cells, metallic zinc has been the popular choice of anode material. In spite of competition from other metals, e.g., magnesium and aluminium, zinc remains the most widely adopted anode material for battery devices. This is because zinc has desirable electrochemical properties, a high electrochemical equivalence, good compatibility with aqueous electrolytes, and low cost [1-6]. The most important of these characteristics is the high hydrogen overvoltage, which can be increased by amalgamation of the zinc. Moreover, by virtue of the uniformity of the anodic attack, the wasteful corrosion of zinc is usually less than that of magnesium or aluminium. The zinc/carbon battery system contains a high-grade zinc electrode to which is added a certain amount of lead and cadmium to improve the mechanical hardening properties, efficiency and stability of the cell. Zinc anodes are also used extensively in the protection of marine structures or buried pipe lines. Anodic polarization investigations on pure zinc using

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aqueous ammonium chloride electrolyte have been performed recently in our laboratory [7]. By contrast, similar studies with zinc alloys are sparse [8, 9].

The work described here relates to the polarization of a zinc-lead-cadmium alloy in different concentrations of ammonium chloride electrolyte over a wide range (5 to 1000 mA, anodic polarization) and narrow range (up to 20 mA, linear polarization) of perturbation conditions. A casting method has been employed to prepare the alloy. The electrode has also been exposed to the corrosive environment of the electrolyte for several days and the resulting corrosion rate has been calculated. Electron micrographs of typical post-immersed electrode samples have been evaluated in order to understand the morphology of the electrode structure.

## Experimental

Weighed quantities of zinc, lead and cadmium were melted together in an electric furnace with continuous stirring. Ammonium chloride was added as the fluxing ingredient during this process. Dross, in the form of oxide, was removed simultaneously. The resultant melt was then transferred to a mould in order to obtain the desired alloy plates. The melt was heated before casting to assist the flow of the molten mixture. The thickness of the alloy plate was 4 mm. The plate was then cut into several 1 cm<sup>2</sup> dimensions. These served as the working electrodes. In order to analyze the alloy composition, atomic absorption spectroscopy (AAS) (Perkin Elmer, model 380, USA) was employed. The amount of zinc present in the alloy was found to be 99.631 wt.% and the compositions of the remaining elements are given in Table 1.

Conventional three-electrode cells, comprising working (zinc alloy), counter (platinum foil) and reference (SCE) electrodes, were employed. A setup consisting of a digital multimeter (Zenith, model ZE 1500), an ammeter (Rometek) and a current regulator (CECRI made) was used for galvanostatic polarization measurements. The linear polarization and Tafel experiments were conducted using a BAS-100 A electrochemical analyser (USA). The zinc electrodes were polished with emery papers and finally degreased with acetone. The measurements were commenced after stabilization of the open-circuit potential.

A conventional weight-loss method was adopted for calculating the corrosion rate of the electrode in the absence of impressed current. Electron micrographs of the pre- and post-immersed electrodes were obtained from a JEOL JSM-35 (CF, Japan) scanning electron microscope. All measurements were performed in triplicate; the reproducibility was  $\pm 2\%$ .

TABLE 1

Composition of Zn-Pb-Cd alloy

Element	Weight percentage (wt.%)
Copper	0.007
Nickel	nil
Antimony	nil
Lead	0.265
Iron	0.010
Cadmium	0.087

The reagents were of AR grade and the solutions were prepared with double-distilled water. Concentrations of ammonium chloride greater than 5.5 N were obtained by heating the respective solutions to 50–60 °C with continuous stirring. All the experiments were carried out at  $28 \pm 1$  °C.

## Results and discussion

### Anodic polarization studies

Figures 1(a) and (b) show the relationship between anodic potential and current density for the Zn–Pb–Cd alloy in different concentrations of ammonium chloride. In 0.5 N solution, the zinc alloy shows abnormal results beyond 730 mA cm<sup>-2</sup>. This is due to the rapid dissolution of the metal and to oxygen evolution. The slope of each linear portion is used to calculate the internal resistance of the electrode/electrolyte interface. It is found that the employment of 0.5 to 3.0 N ammonium chloride solution

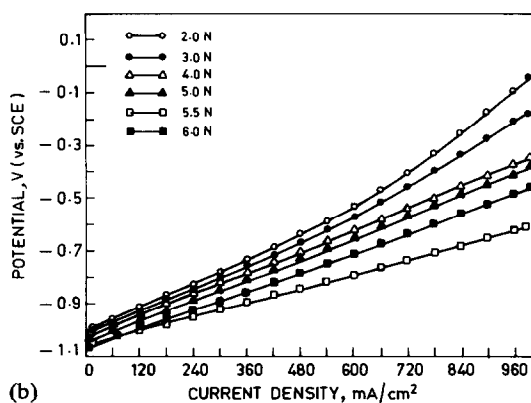
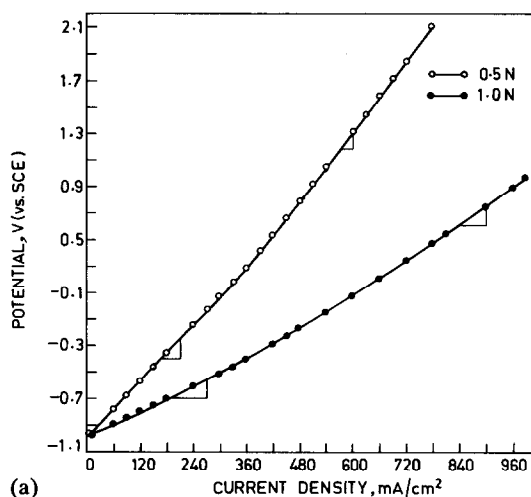


Fig. 1. Potential vs. current density for the Zn–Pb–Cd alloy in (a) 0.5 and 1.0 N  $\text{NH}_4\text{Cl}$ , and (b) in different concentrations of  $\text{NH}_4\text{Cl}$ .

brings about a split in the internal resistance between two current density regions. By contrast, a single straight line is obtained for higher concentrations of ammonium chloride solution viz., 4.0 to 6.0 N (Fig. 1(b)).

The corresponding internal resistance data of the zinc alloy at different current densities are given in Table 2. It may be noticed that the internal resistance values increase in the regions of higher current density. This is the case only at the lower concentrations, i.e., below 3.0 N. Accordingly, it would appear that these concentrations promote non-uniform polarization in the current density range used in this investigation.

Derivative results that show the relationship between internal resistance or anodic potential and concentration are presented in Figs. 2 and 3, respectively. It is evident that both the internal resistance and the anodic potential of the electrode fall sharply for electrolyte concentrations up to 2.0 N. These two parameters then decrease gradually with further increase in the concentration. The data shown in Fig. 3 correspond to a constant-current density of  $645 \text{ mA cm}^{-2}$ . The graph obtained at lower current densities, viz., 5 to  $330 \text{ mA cm}^{-2}$ , follows a similar pattern, and therefore, are not shown here. The variation of electrode potential with electrolyte concentration is shown in Table 3. Beyond 5.5 N, the electrode potential shifts to more positive values. The electrode potential and internal resistance are found to be more positive at lower concentrations (e.g., 0.5 and 1.0 N) when compared with pure zinc. At higher concentrations, i.e., above 2.0 N, the alloy possesses a more negative potential and less internal resistance (Fig. 2). These data indicate that the alloy electrode is a better choice for Leclanché cells than pure zinc.

The breaks in the potential and internal-resistance curves beyond 5.5 N show that the electrolyte could have suffered some physical change that results in an increase in the resistance of the system. Crystallization studies showed that the electrolyte exists

TABLE 2

Comparative data of internal resistance of a Zn-Pb-Cd electrode in various concentrations of  $\text{NH}_4\text{Cl}$  at different current densities

Concentration (N)	Current density ( $\text{mA cm}^{-2}$ )	Internal resistance ( $\Omega \text{ cm}^{-2}$ )
0.5	5-360	3.57
	420-780	4.33
1.0	5-330	1.61
	570-1000	2.27
2.0	5-570	0.83
	837-1000	1.27
3.0	5-486	0.74
	660-1000	1.01
4.0	5-1000	0.69
5.0	5-1000	0.65
5.3	5-1000	0.57
5.5	5-1000	0.45
5.7	5-1000	0.55
6.0	5-1000	0.61

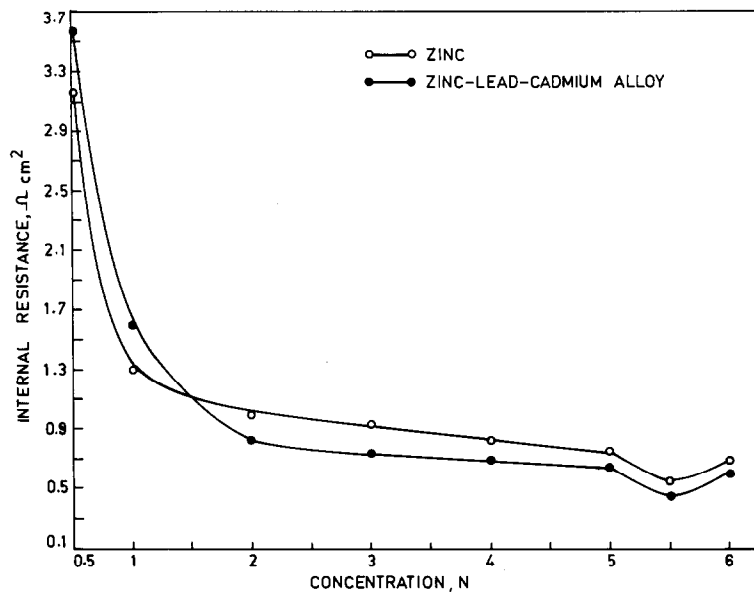


Fig. 2. Dependence of internal resistance with concentration.

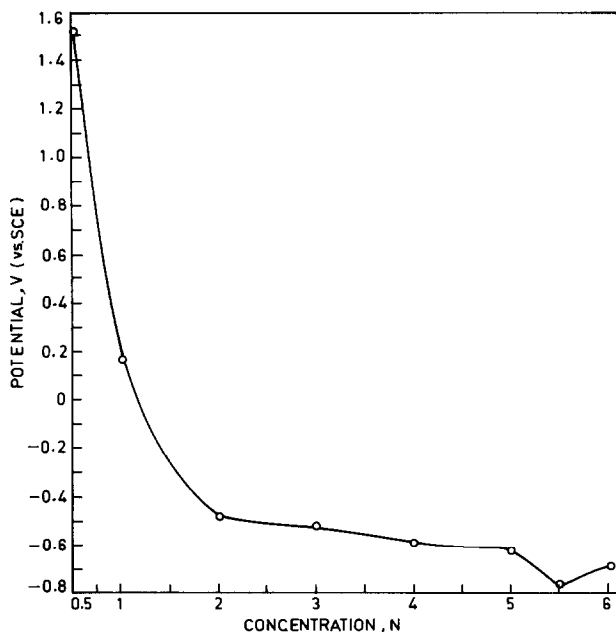


Fig. 3. Dependence of electrode potential with electrolyte concentration for the Zn-Pb-Cd alloy at a constant current density of  $645 \text{ mA cm}^{-2}$ .

TABLE 3

Variation in the electrode potential against  $\text{NH}_4\text{Cl}$  concentration at a constant current density of  $645 \text{ mA cm}^{-2}$

Concentration (N)	Potential (V)
0.5	+1.52
1.0	+0.17
2.0	-0.48
3.0	-0.52
4.0	-0.59
5.0	-0.62
5.3	-0.71
5.5	-0.77
5.7	-0.64
6.0	-0.68

in the solution phase up to a concentration of 5.5 N. Above this value, crystals of ammonium chloride precipitate from the solution at a rate that increases with the concentration of the electrolyte at 50–60 °C. This crystallization behaviour clearly shows that the break in the curves is due to a minimum polarization at 5.5 N concentration. At the same time, the ohmic resistance is likely to be increased because of the build-up in crystals.

#### *Linear polarization and Tafel studies*

Linear polarization and Tafel investigations were carried out by disturbing the equilibrium conditions of the system by  $\pm 20$  and 500 mV, respectively. The polarization resistance ( $R_p = E/I$ ) for different concentrations of  $\text{NH}_4\text{Cl}$  was calculated. The exchange current density ( $i_0$ ) was determined from the following expression:

$$i_0 = RT/nF \times 1/R_p \quad (1)$$

The value of  $i_0$  was also determined from a constant potential range of 500 mV in the Tafel plot. The parameters thus obtained are listed in Table 4. Typical examples of the linear polarization and Tafel plots are given in Figs. 4 and 5, respectively. The results show that an increase in the concentration of ammonium chloride from 0.5 to 5.5 N brings about a gradual increase in the value of  $i_0$ . Above 5.5 N, this trend is reversed, as expected from the findings discussed above. The  $i_0$  data obtained by the linear polarization method are similar to those obtained by the Tafel method.

#### *Corrosion-rate calculations*

The corrosion rate of the zinc alloy was evaluated by exposure of the electrode to a solution of 0.5 N ammonium chloride for 410 h. The corrosion products were removed with 15%  $\text{NH}_4\text{OH}$ . The weight loss was 0.0500 g. The following formula was used to calculate the corrosion rate of the sample:

$$\text{rate(mpy)} = 534W/DAT \quad (2)$$

where: mpy is mils penetration per year; W is the weight; D is the density ( $7.14 \text{ g cm}^{-3}$ ); A is the area; T is the exposure time.

TABLE 4

Polarization resistance ( $R_p$ ) and exchange current density ( $i_0$ ) for a Zn-Pb-Cd electrode at different  $\text{NH}_4\text{Cl}$  concentrations

Concentration (N)	$R_p$ ( $\Omega$ )	$i_0$ ( $\times 10^4$ ) ( $\text{A cm}^{-2}$ )	
		By linear polarization	By Tafel method
0.5	58	2.19	2.70
1.0	52	2.44	2.94
2.0	48	2.65	3.20
3.0	45	2.82	3.73
4.0	42	3.02	3.94
5.0	38	3.34	4.25
5.3	32	3.40	4.95
5.5	29	4.38	6.00
5.7	34	3.74	4.68
6.0	37	3.43	4.15

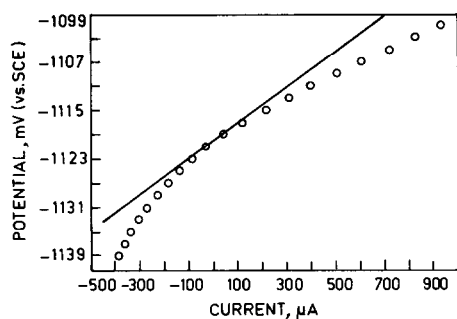


Fig. 4. Typical linear polarization plot of the Zn-Pb-Cd electrode in 5.5 N  $\text{NH}_4\text{Cl}$  solution.

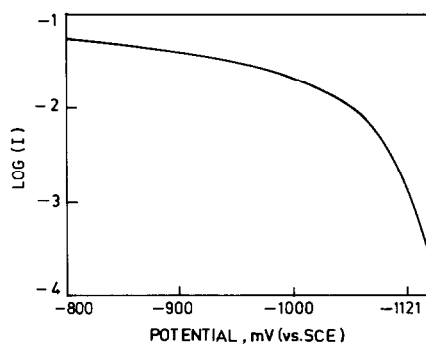


Fig. 5. Typical Tafel plot of the Zn-Pb-Cd electrode in 5.5 N  $\text{NH}_4\text{Cl}$  solution.

The corrosion rate of the alloy was found to be 58.84 mpy. This value is larger than that for pure zinc, viz., 49.66 mpy [7]. The observed difference in rate is due to the fact that more galvanic couples are formed in the alloy system. The half-cell potential for the zinc alloy was recorded daily and was found to be virtually constant over the 410-h period.

#### SEM analysis

An electron micrograph of the pre-immersed surface, Fig. 6, shows a more or less uniformly distributed segregated pattern. This is indicative of the presence of a multi-component system, viz.,  $\text{Zn-Pb}_x\text{-Cd}_y$ . By contrast, the micrograph of the post-immersed Zn-Pb-Cd alloy (Fig. 7) reveals that the grain boundaries are attacked. The corroded profile remains uniform and the corrosion distribution comprises two distinct metallurgical phases, viz., Zn-Pb and Zn-Cd. The micrograph does not show any evidence of pit formation.

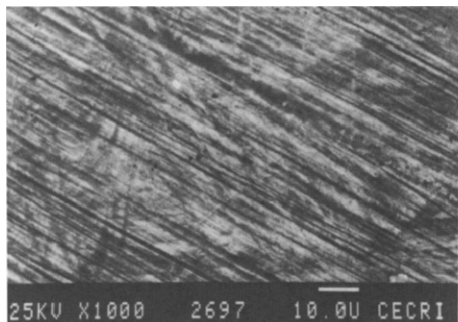


Fig. 6. Electron micrograph of pre-immersed Zn-Pb-Cd electrode.

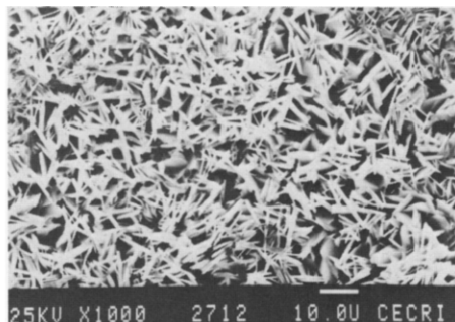


Fig. 7. Electron micrograph of post-immersed Zn-Pb-Cd electrode.

### Conclusions

1. The effective concentration of ammonium chloride is 5.5 N. At this value, the exchange current density is  $4.4$  to  $6.0 \times 10^{-4} \text{ A cm}^{-2}$ .
2. A zinc-lead-cadmium electrode has less internal resistance, i.e.,  $0.45 \Omega \text{ cm}^{-2}$  compared with  $0.56 \Omega \text{ cm}^{-2}$  for a zinc electrode in 5.5 N ammonium chloride.
3. A zinc-lead-cadmium electrode exhibits a more negative potential than pure zinc, particularly at high concentrations of ammonium chloride solution, i.e., 2.0 N.
4. The corrosion rate of the alloy system in a typical ammonium chloride solution (i.e., 5.5 N) is 58.84 mpy.

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