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# *Corrosion in alkali hydroxide solutions of electrolytic zinc powder containing codeposited lead*

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The corrosion rate of electrolytic Zn sponge in alkaline solutions is controlled by codeposited Pb in concentrations from 0·2–0·5%. It appears that codeposited lead in this respect is as good as mercury but has the advantages of being cheaper and less toxic. The Zn sponge containing codeposited Pb offers the additional advantage of having a highly developed surface area so that the porous electrodes pressed with such a sponge can be discharged at higher rates.

The effect of KOH concentration on the corrosion rate of Zn sponge with and without Pb is explained in terms of the different mechanisms of the hydrogen evolution reaction on the Fe inclusions on the one hand, and on pure Zn on the other. An empirical equation for the approximate estimation of the corrosion rate of Zn sponge in 10 N KOH at 50° C as a function of Pb and Fe content in the sponge is presented.

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## 1. Introduction

Modern high performance zinc alkaline batteries are unthinkable without the use of porous zinc electrodes. The high specific surface area of the porous structure permits a large anodic c.d. without passivation even at comparatively low temperatures. Unfortunately this advantage has to be paid for by an increased corrosion rate or self-discharge reaction. Thus the problem of preventing corrosion of the porous zinc electrode in alkaline solutions arises. In practice, irrespective of the initial material (Zn or ZnO), the electrodes are manufactured with the addition of 1–4% Hg.

Despite its thermodynamic instability in alkaline media, pure zinc dissolves very slowly on account of kinetic hindrances. Of the two possible cathodic reactions:

$$O_2 + 2H_2O + 4e = 4OH^- \qquad (I)$$

$$2H_2O + 2e = H_2 + 2OH^-, \qquad (II)$$

either of which is a prerequisite for the anodic dissolution reaction to proceed, the first one is hampered by the low solubility of oxygen in concentrated alkaline solutions, while the second is retarded by the high hydrogen overpotential on the zinc surface. Under actual conditions of a battery operation the corrosion through oxygen depolarization is negligible, so that the efforts are directed towards lowering the rate of reaction II.

So far no inorganic or organic inhibitor added to the electrolyte has proved to be effective and the usual practice is to employ zinc essentially free of metallic impurities (Fe, Cu and Ni) and to add metals (or their oxides) with a higher hydrogen overvoltage (Hg or Pb). Zinc materials with 0·0005% Fe are readily accessible but contamination during electrode processing is not excluded, so that concentrations of Fe up to 0·005% in the final product have to be taken into account.

The effect of Hg on the corrosion rate of Zn in concentrated KOH and NaOH solutions has been studied by a number of workers [1–7]. Less information is available on the influence of Pb, which offers the dual advantage of being less expensive and less toxic than Hg.

A method for the electrolytic deposition of Zn sponge for porous zinc electrodes was recently developed in this laboratory [8, 9]. The electrolysis is carried out in comparatively concentrated zincate solutions containing a definite concentration of plumbate ions, as a result of which a sponge with a fine-grained dendritic structure is deposited. The electrodes pressed from this sponge are mechanically rigid with a porosity 75–80%. Their anodic efficiency at 60 mA $cm^{-2}$ is 75–80%, and without Hg added their self-discharge was found to be within the permissible limits. The present paper presents some data on the corrosion rate of zinc powder prepared by the above-mentioned method as a function of its Pb content, Fe contamination, and KOH concentration.

## 2. Experimental

### 2.1. *Zinc sponge preparation*

The zinc sponge deposited from the plumbate containing electrolyte was washed in $CO_2$-saturated distilled water so as to avoid its oxidation and dried. Microscopic observations revealed a fine dendritic structure (Fig. 1).* Sedimentation analysis of samples containing 0·1–0·2% Pb showed a maximum particle size between 7 and 12 $\mu$m. Depending on the Pb concentration in the sponge, the specific surface area varied from 0·3–8 $m^2$ $g^{-1}$. In order to obtain samples with different Fe contamination, zinc anodes of various purities were used, while for the highest Fe content an additional steel anode was employed. Lead was added to the electrolyte in the form of acetate. Since both Zn and Pb were deposited under diffusion limiting conditions, the ratio Zn/Pb in the sponge corresponded to that in the solution. The analysis of Pb in the sponge was performed by atomic absorption spectrophotometry (Unicam SP-90-B) and that of Fe by the spectrophotometric measurement of the sulphosalycilate complex.

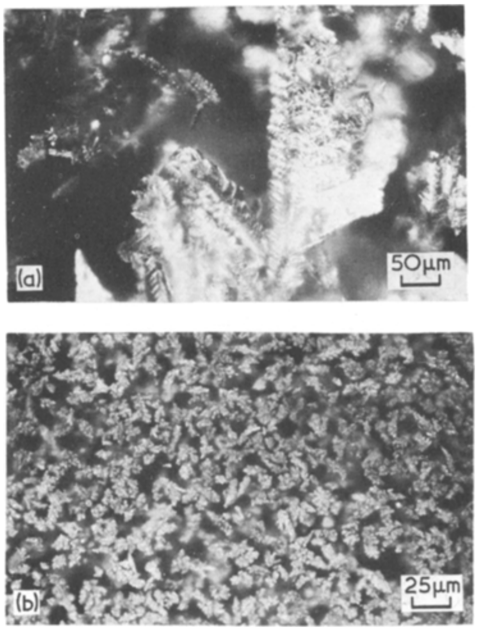

Fig. 1. Microphotographs of electrolytic zinc powders containing (a) 0·005% Pb; (b) 0·2% Pb.

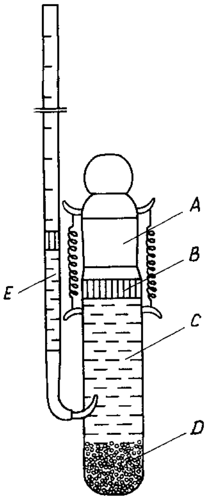

Fig. 2. Glass vessel for corrosion measurements. A–ground glass stopper; B–transformer oil layer; C–electrolyte; D–zinc powder sample; E–pipette.

### 2.2. *Corrosion measurements*

The corrosion rate as in most previous investigations was determined by the hydrogen evolution method under conditions which eliminated oxygen access. A glass vessel (Fig. 2) tightly closed by a ground glass stopper coated with silicone grease was used in all measurements. The hermeticity of each vessel was periodically checked. The hydrogen evolved from the sample was trapped in the vessel, and the displaced solution volume was measured in a calibrated pipette (2 ml). To avoid electrolyte creeping into the stopper, a layer of transformer oil was poured over the test alkaline solution. The experiments were performed at least in duplicate with 0·1–0·5 g of Zn powder at 50 ∓ 0·5° C in an air thermostat. The corrosion rate was expressed in ml of $H_2$ (at normal temperature and pressure) per gram Zn per hour.

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* The effect of lead on the structure of the Zn sponge has been studied extensively [8–12].

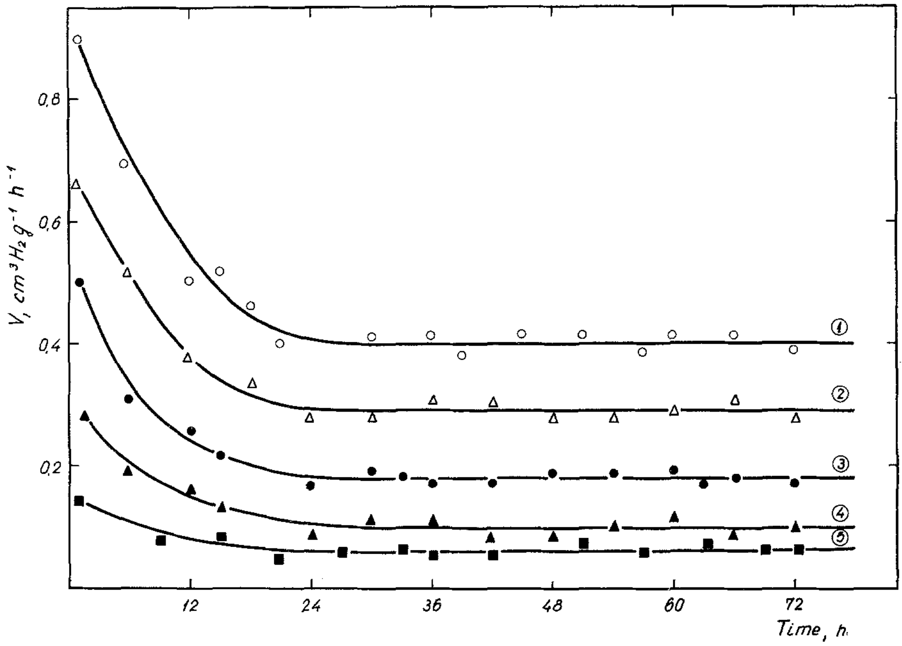

Fig. 3. Time dependence of the corrosion rate ($V$) at 50°C in 10 N KOH of zinc samples containing 0·008–0·009% Fe doped with: 1–0·1; 2–0·2; 3–0·3; 4–0·4; 5–0·5% Pb.

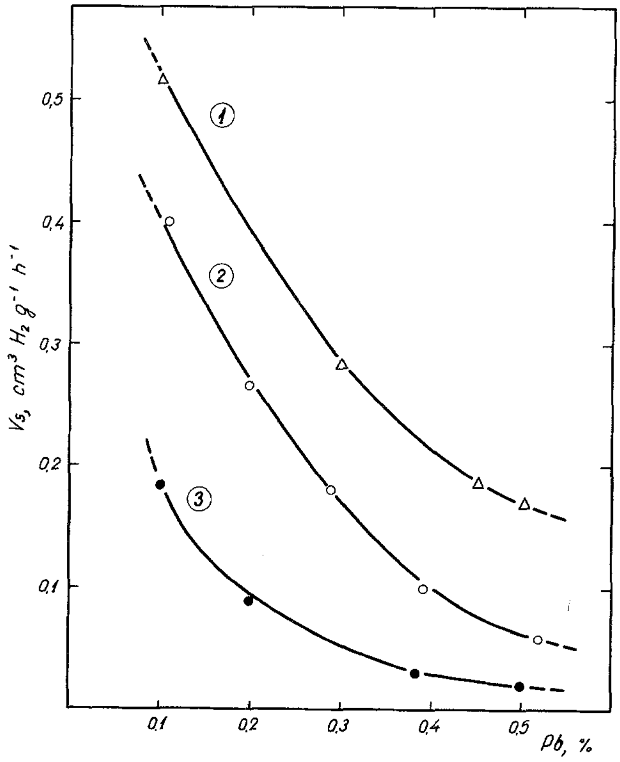

Fig. 4. Corrosion rate ($V_s$) of zinc powders at 50° C with different Fe contaminations as a function of Pb concentration. 1–0·012; 2–0·007; 3–0·001% Fe.

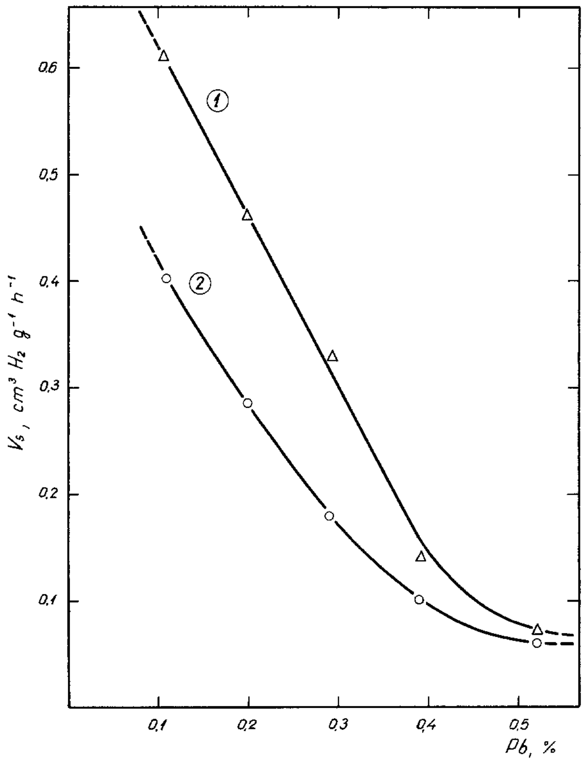

Fig. 5. Corrosion rate ($V_s$) of zinc powders in 7 and 10 N KOH as a function of Pb concentration (Fe = 0·009%) at 50° C. 1–7 N KOH, 2–10 N KOH.

Corrections were made for the solution column height in the pipette as well as for the saturated vapour pressure over the KOH solution.

## 3. Results and discussion

Fig. 3 illustrates the time dependence of the corrosion rate of five Zn powder samples with different Pb concentrations. The initial high rate rapidly decays and within 15–18 h a steady corrosion rate $V_s$ is established, which remains constant over three or more days. The rate values given always refer to the steady state conditions reached 24 h after the beginning of the experiment, unless otherwise stated.

The relationship between $V_s$ and the concentration of Pb in the Zn samples at three different Fe levels in a 10 N KOH solution is shown in Fig. 4. The corrosion rate falls almost exponentially with the Pb increase at all Fe levels. The effect of Pb at two KOH concentrations (7 and 10 N) is presented in Fig. 5. It appears that the increase of KOH concentration in this region leads to a reduction in the corrosion rate. The effect of KOH concentration, however, gradually diminishes with the increase of Pb content and practically disappears at 0·5% Pb.

The effect of KOH concentration between 5 and 10 N on the corrosion rate ($V_s$) of Zn powder samples containing 0·3% Pb with three different Fe concentrations is seen in Fig. 6. At lower Fe levels, the increase of KOH concentration has no effect on $V_s$, while at the higher levels there is a noticeable decrease.

A similar influence of the KOH concentration on the corrosion rate of dosed and undosed Zn samples has been reported earlier [3, 4], but no explanation has been proposed. A reasonable explanation seems possible if one takes into account that in dosed samples the hydrogen evolution reaction (h.e.r.) takes place mainly on the Fe inclusions. Despite the much smaller partial surface area of the Fe inclusions the partial current of the h.e.r. on them is significant because of the much larger exchange c.d.: $6 \times 10^{-5}$ A cm$^{-2}$ on Fe [10] and $10^{-10}$ A cm$^{-2}$ on Zn [11]. As shown by Platonova and Levina [14], the increase of KOH concentration from 4·8–10·5 N at $i$ = constant leads to an increase of the $H_2$ overvoltage on the Fe electrode. When Pb or Hg is added to the Zn sample, the Fe cathodes are substantially deactivated and if the effect is deep enough, the h.e.r. will occur predominantly on the active centres of Zn. In the case of high purity Zn, Iofa *et al.* [13] have found that the increase of KOH concentration from 5–10 N brings about only a slight rise in the $H_2$ overvoltage. Thus the different effect of KOH concentration on the corrosion rate of dosed and undosed Zn reported here and earlier [3, 4] seems to find a logical interpretation in terms of the different mechanism of the h.e.r. on Zn and Fe.

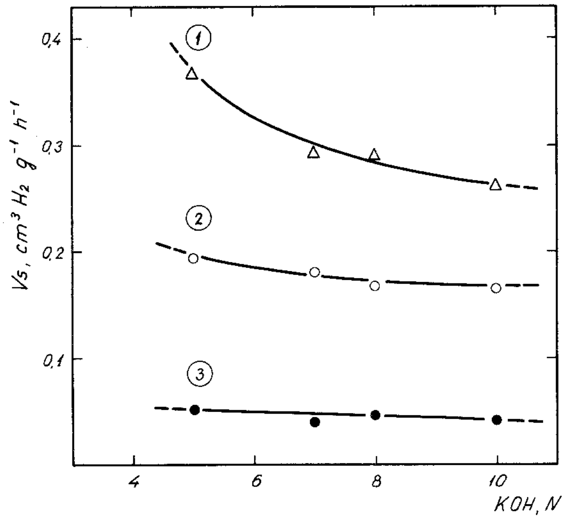

Fig. 6. Effect of KOH concentration on corrosion rate ($V_s$) of zinc samples with 0·3% Pb with different Fe contaminations. 1 – 0·012; 2 – 0·007; 3 – 0·001% Fe.

Fig. 7 presents the effect of Pb concentration on $V_s$ at three Fe levels in log–log coordinates. The linearity of the plots for Pb 0·1% and the similarity of their slopes for Fe 0·013% make it possible to derive an approximate empirical equation

*Table 1. Corrosion rate of zinc in alkaline solutions*

| *Characteristics of the tested materials* | | | | | *Corrosion conditions* | | | |
|---|---|---|---|---|---|---|---|---|
| | *Purity of the initial material* | | *Additions (%)* | | | *Temperature (°C)* | *Corrosion rate, $V_s$* | |
| *Type* | *Zn* | *Fe* | *Pb* | *Hg* | *Electrolyte* | | ($cm^3$ $H_2$ $g^{-1}$ $h^{-1}$) | *Reference* |
| a | 99·95 | 0·017 | | – | 4·3 N NaOH+ | | 0·363 | |
| | | | – | 0·5 | 2·7 N KOH+ | 50 | 0·018 | 1 |
| | | | | 1·0 | 0·6 M ZnO | | 0·014 | |
| b | 99·6 | 0·002 | | – | 11 N KOH+ | | 0·080 | |
| | | | 0·045 | 1·0 | | 45 | 0·017 | 5 |
| | | | | 10·0 | 1 M ZnO | | 0·005 | |
| b | ND | ND | – | 5·0 | 9·15 N KOH | 40 | 0·050 | 6 |
| c | ZnO | ND | 2·0 | – | 7 N KOH | | 0·040* | |
| | | | – | 2·0 | | 50 | 0·085* | 7 |
| | | | | 4·0 | 10 N KOH | | 0·025* | |
| d | 99·95 | 0·012 | | | | | 0·180 | |
| | 99·975 | 0·007 | 0·5 | – | 10 N KOH | 50 | 0·060 | Present results |
| | 99·995 | 0·001 | | | | | 0·020 | |

(a) Pasted electrodes prepared from metallurgical zinc powder.
(b) Metallurgical zinc powder.
(c) Zinc electrodes prepared by reduction of mixtures of ZnO, PbO and HgO.
(d) Electrolytic zinc powder with codeposited lead.
* These values are interpolated.
ND – no data.

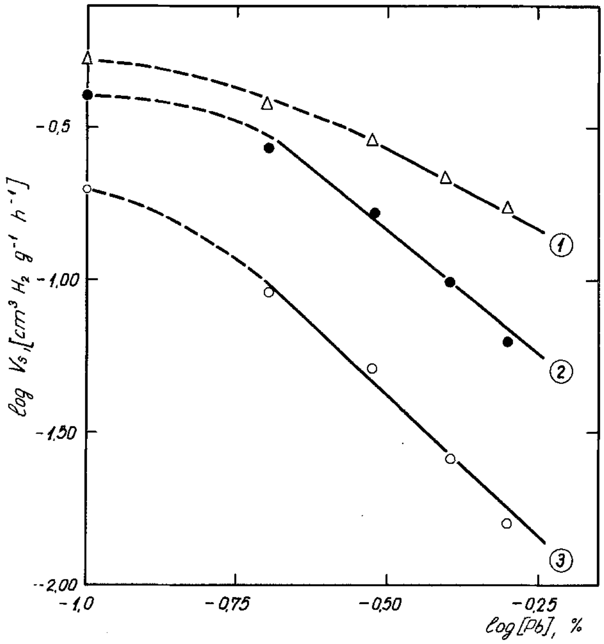

Fig. 7. Log–log dependence of Pb concentration on $V_s$ in 10 N KOH at 50° C of samples with: 1–0·012; 2–0·007; 3–0·001% Fe.

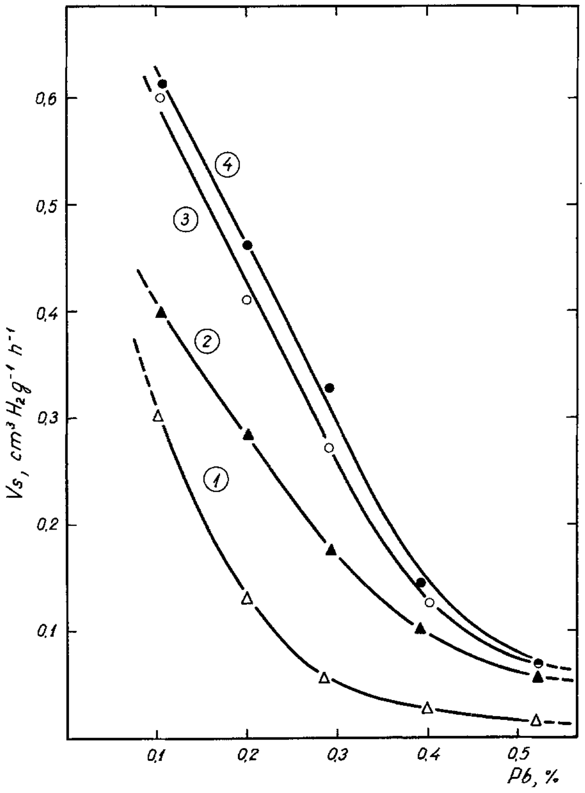

Fig. 8. Effect of Pb concentration on the corrosion rate ($V_s$) at 50° C of samples with 0·008% Fe at different KOH and NaOH concentrations. 1–10 N NaOH; 2–10 N KOH; 3–7 N NaOH; 4–7 N KOH.

for the estimation of $V_s$ in 10 N KOH at 50° C as a function of the concentrations of Pb and Fe:

$$\log V_s = -1{\cdot}68 \log [\mathrm{Pb}] + 1{\cdot}02 \log [\mathrm{Fe}] + 0{\cdot}49$$

where concentrations are in weight % and $V_s$ in ml. $H_2$ $g^{-1}$ $h^{-1}$. Within the limits: $0{\cdot}003 < \mathrm{Fe} < 0{\cdot}010\%$ and $0{\cdot}15 < \mathrm{Pb} < 0{\cdot}5\%$ the accuracy is $\mp 25\%$. This equation is of course valid only in the case where other cathodic impurities such as Cu and Ni are less than 0·005%.

From the practical point of view it is also interesting to know the effect of substituting KOH for NaOH on the corrosion rate of the Zn powder. As seen in Fig. 8 a marked decrease of $V_s$ due to the change of the electrolyte is observed only at the higher concentration (10 N), while at the lower one the difference is insignificant. The effect is due obviously to the higher $OH^-$ activity in the KOH solutions than in the NaOH solutions at equal concentrations. The effect of Pb in NaOH solutions is however similar to that in KOH.

Table 1 presents comparative data on Zn corrosion in KOH solutions as reported by different authors. Data are also given for the composition of the Zn samples used in the test and on the conditions under which the corrosion rates are assessed. Efforts were made to present as much as possible similar corrosion conditions. In some cases, graphic data had to be extrapolated. It is seen from Table 1 that the inhibition effect of Pb on the corrosion rate of Zn samples of equal purity (%Fe) is the same or even better than that of Hg at equal concentrations. On the other hand the effect of Pb added as PbO [7] is considerably lower than that of Pb codeposited with the Zn sponge, irrespective of the significantly increased specific surface area due to the influence of the Pb addition. This result suggests that during the sponge electrodeposition the lead is uniformly deposited over the larger Zn dendrites thus blocking the sites active in the corrosion process, e.g. Fe inclusions, dendrite tips, etc. [9].

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