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Electrochemical behaviour of a zinc electrode in 8 M KOH under pulsed potential loading

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Electrodeposition of zinc on zinc plates has been investigated in 8 M KOH. Zincate solutions were obtained by dissolution of ZnO is hot 20 M KOH. Direct current and pulsed current electrodepositions were performed and the deposits observed by SEM. Spongy and dendritic deposits are avoided when using pulsed current technique. A 1 : 8 to 1 : 10 ratio for pulse time on rest time is shown to be efficient. The instantaneous current density may be as high as $-1.3\ \mathrm{A\ cm^{-2}}$ provided the pulse is short enough so that the concentration profile is not too much perturbated. It is shown that a slight dissolution occuring during the rest time is highly accurate in obtaining compact, adherent and well crystallized deposit. Additives such as lead or bismuth induce very small crystallites, and are recommended to improve the compactness. Organic compounds such as fluorinated surfactants are also efficient but the compactness is a little less as above.

1. Introduction

The zinc electrode has been widely studied in alkaline media because of its possible use in light rechargeable batteries and as a power source for electrical vehicles [1–4]. Nevertheless, it has been noticed that electrodeposition of zinc leads to three kinds of deposits: spongy, compact and dendritic, according to the current density [5–11]. Dendritic electrocrystallization has been previously studied by Bockris *et al.* [11–12] and Diggle *et al.* [13] using galvanostatic and potentiostatic techniques, and the effect of a flowing electrolyte was investigated by Naybour [14].

Many attempts to understand the dendritic growth have been made in order to evaluate the critical overpotential where dendritic phenomenon appear, and the potential range where dendrites grow rapidly. This problem concerns metals such as silver and lead as well as zinc in KOH solution [15–18].

Another way of limiting dendritic growth is the use of alternating superimposed current [19] or pulsed current [20–25]. The concentration profiles in the vicinity of the electrode were discussed by Ibl [26]. The choice of the pulse parameters has been widely discussed in several papers [27–35] and fundamental aspects of pulse plating have been investigated by Popov *et al.* [31–33], Hosokawa *et al.* [34] and Chin [35].

Additives, both inorganic and organic such as thiocompounds [36] and fluorinated surfactants [37], have been tested to limit dendritic growth.

In addition, spongy deposits have received attention because it is necessary to avoid these in order to limit the brittleness of the electrode. Recently Wiart *et al.* described anodically dissolved zinc (ADZ) and demonstrated its role in surface modification of the electrode by impedance measurements [34].

The papers dealing with the zinc electrode are too numerous to be reviewed exhaustively here. However, pulsed currents have received some attention in the last ten years. The aim of the present paper is to determine the pulse parameter values leading to a non-dendritic deposit on zinc plates immersed in 8 M KOH. These parameters include the pulse time, the rest time, the current densities during both the pulse and rest time, and the zincate concentration.

Additives (both organic and inorganic) were introduced to the medium in order to obtain very adherent and finely crystallized deposits. The hardness of these deposits was recorded. In addition the multicycles of charge and discharge were applied with a home-made potentiostat.

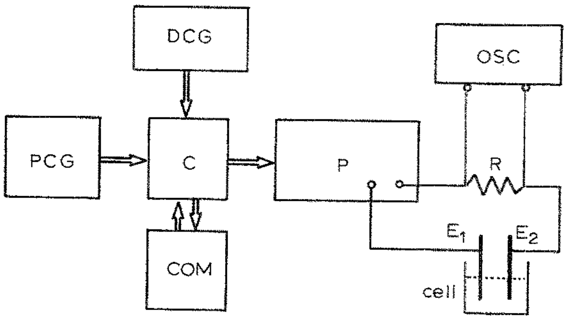

Fig. 1. Block diagram of the electrical circuitry for multi-cycles of charge and discharge, P: potentiostat, C: commutator, COMP: computer, PCG: pulse current generator, DCG; direct current generator, OSC: oscilloscope, R: 1.32 Ω resistance, E1 and E2: zinc electrodes.

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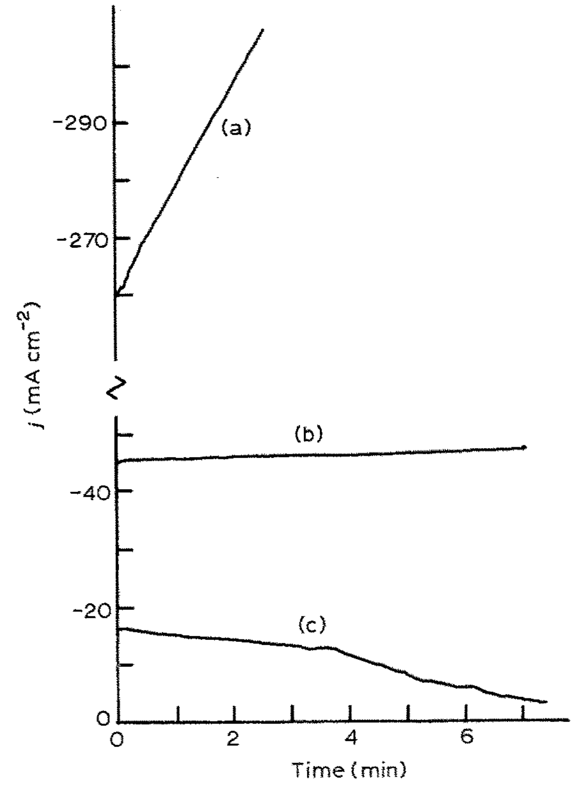

Fig. 2. Variation of the current density, at a fixed initial value of the potential, as a function of time. Initial current density: (a) −270, (b) −45, (c) −18 mA cm^{-2}.

2. Experimental details

Dissolution of ZnO up to 3 M was achieved by heating a 20 M KOH solution to 80° C. Approximately 2% of sodium silicate was added in order to stabilize the solution. Then after cooling to room temperature, appropriate dilution was made to adjust the KOH concentration to 8 M. All the reagents were obtained from PROLABO (France) and were of analytical grade. The zinc electrode was a 1 cm wide, 1 mm thick and 20 cm long zinc plate of 99.5% purity. Industrial zinc was preferred in this study. Comparison with high purity zinc rod (99.99%) yielded the same results.

A typical experiment was performed by immersing two zinc plate electrodes 1 cm in solution. The two plates were parallel and separated by a spacer of 1.5 cm width. A PJT 24-1 fast potentiostat and a GSTP3 signal generator (TACUSSEL, France) were used to generate the potential pulses. The magnitudes of both potential and currents were simultaneously recorded with a 5115 oscilloscope (TEKTRONIX, USA). Three ‘plug-ins’ were added to the basic oscilloscope: two amplifiers and one base time.

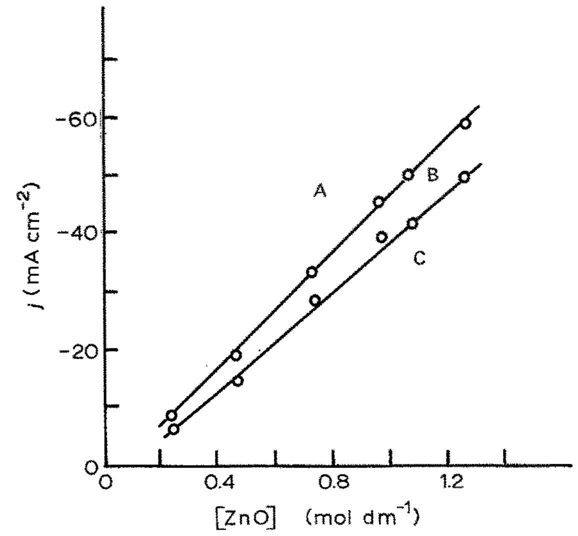

Fig. 3. Morphological aspect of zinc deposit as a function of both current density and zincate concentration. A: dendritic range, B: compact range, C: spongy range. (Points are the boundary values between two ranges.)

For multicycle charge and discharge the block diagram of the apparatus is given in Fig. 1. (The computer was a 64 Commodore)

The hardness of the deposits was measured by using a compactness device, model DY 14 (Adamel-Lhomargy, France). The stainless steel tool had a 0.1963 cm^2 cross section.

A scanning electron microscope (Philips, SEM 512) was used to examine the surfaces of the deposits.

All experiments were performed without nitrogen bubbling at room temperature.

3. Results and discussion

In order to compare deposits obtained on the zinc electrodes by both direct constant current and pulsed potential techniques, several experiments were performed in a 1.08 M ZnO and 8 M KOH bath by simply changing the initial current density. It may be observed from Fig. 2 that a spongy deposit was seen for low current density, i.e. $j - 35\,\mathrm{mA\,cm^{-2}}$. In this case, the applied potential being constant, there was a

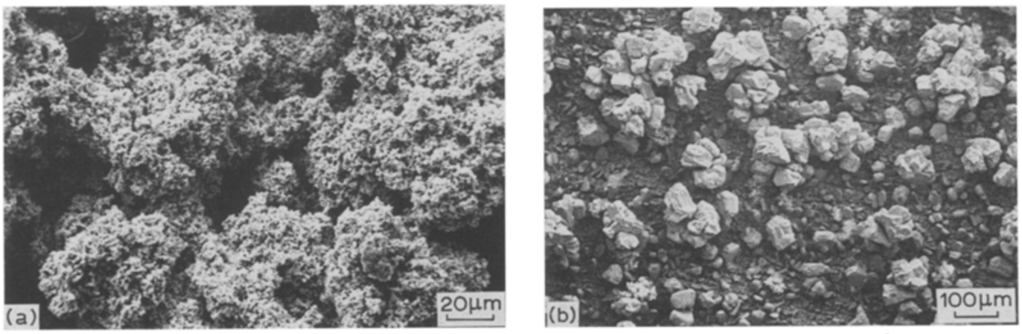

Fig. 4. SEM micrographs of zinc deposit obtained with direct current: (a) compact deposit with −45 mA cm^{-2} current density; (b) dendritic deposit with −270 mA cm^{-2} current density.

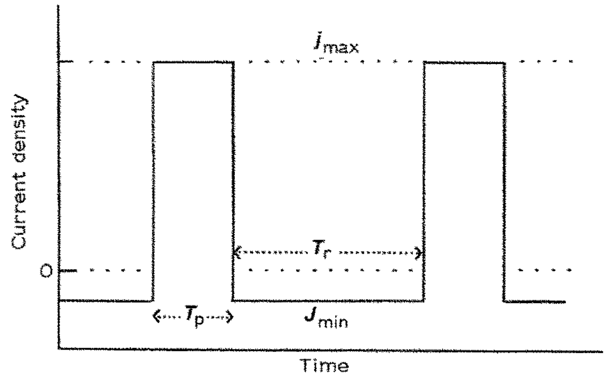

Fig. 5. Shape of the pulses and pulse parameters.

progressive decrease of the current as the thickness of the deposit increased. A uniform deposit was observed for current densities ranging from -40 to $-50\,\mathrm{mA\,cm^{-2}}$, the current being constant. For initial large values of current density, dendritic deposits were observed and the current increased immediately. Observable dendrites appeared randomly at the zinc surface and then fell, accumulating at the bottom of the cell.

From a large number of experiments performed with several initial values of both the constant potential and the ZnO concentration, it was noticed that the range where deposits were compact was very narrow. (Fig. 3).

Observations of the zinc surface by SEM in the above cases led to detection of strong morphological changes. (Fig. 4).

For experiments with pulsed potential steps we considered four important parameters: (i) the pulse time to rest time ratio; (ii) the pulse duration; (iii) the frequency of the pulses; and (iv) the applied current between two pulses. (Fig. 5). In fact a large number of experiments were necessary to evaluate the effects of each parameter, but it was relatively easy to shorten these investigations by considering that a pulse was evidently short, the rest time being longer in order to let the disturbed concentration profile become approximately identical to that before the pulse.

After several preliminary tests, we initially used a $T_{\mathrm{pulse}}/T_{\mathrm{rest}}$ ratio (T_p/T_r) of 0.1, and a pulse current density ranging from -0.5 to $-1.15\,\mathrm{A\,cm^{-2}}$. During the rest time we chose to apply a small anodic current of $+0.02$ to $+0.05\,\mathrm{A\,cm^{-2}}$ in order to obtain slight dissolution of the deposit obtained during the preceding pulse. This procedure avoided a large disturbance of the concentration profile when the next pulse was applied. The usual progressive lack of zincate, observed both with direct current and pulsed current with a null current during the rest time, was compensated favourably. It was expected that this procedure would be efficient in avoiding dendritic growth as illustrated below.

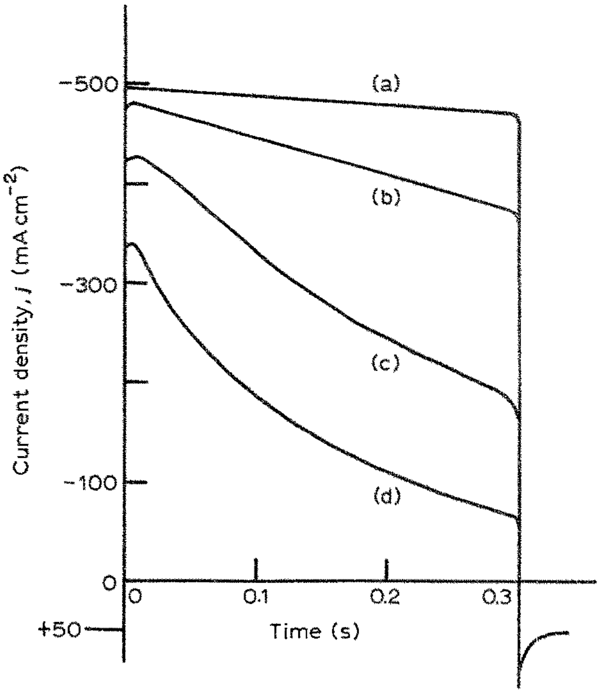

Fig. 6. Influence of the rest time on the current density during the next pulse: (a) 3s, (b) 1s, (c) 0.3s, and (d) 0.1s.

Table 1 lists typical data in accordance with the above remarks. Although the current efficiency was interesting, the nature of the deposits was strongly dependent on the sign of the direct current flowing during the rest time. For electrodes 1 and 2 the deposit was of very fine crystals with good adhesion and compactness. Electrode 3 exhibited some dendrites, in the case of electrodes 4 and 5 dendrites were numerous, and the deposits were becoming powdery.

Table 1. Morphology and yield of the electrodeposits according to the value of J_{min} applied during the rest time. Other parameters: $J_{max} = -1.03\,A\,cm^{-2}$; $T_{pulse} = 0.3\,s$; $T_{rest} = 3\,s$

Sample	*1*	*2*	*3*	*4*	*5*
$J_{\min}$ (mA cm^{-2})	+50	+25	0	−25	−50
Zinc deposit Experimental (g)	0.0515	0.0827	0.1076	0.1366	0.1597
Zinc deposit Theoretical (g)	0.0592	0.0869	0.1145	0.1422	0.1699
Yield (%)	87	95.1	94	96	94
Morphology	Very fine Compact Shiny	Fine Compact Shiny	Rough Compact	Spongy	Spongy Dendrites

Table 2. Morphology and yields of the electrodeposit according to the value of J_{max} applied during the pulse time. Other parameters: $J_{min} = +50\,mA\,cm^{-2}$; $T_{pulse} = 0.3\,s$; $T_{rest} = 3\,s$

Sample	J_{max} ($mA\,cm^{-2}$)	*Yield* (%)	*Morphology*
1	483	–	Slight dissolution
2	637	62.6	Compact. Finely crystallized
3	734	82.3	*ibid.*
4	888	88.6	*ibid.*
5	985	84.7	*ibid.*
6	1109	96.8	*ibid.*

Table 3. Morphology and yield of the electrodeposit according to the T_{pulse} to T_{rest} ratio

Sample	T_p/T_r	*Yield* (%)	*Morphology*
1	0.1/1	92.9	Finely crystallized. Compact
2	0.2/2	81.9	*ibid.*
3	0.3/3	88.9	*ibid.*
4	0.5/5	92.6	*ibid.*
5	0.7/7	88.2	*ibid.*
6	1/10	95.3	*ibid.*
7	2/20	71.6	Large crystallites. Rough.
8	3/30	50	Spongy. Friable. Non-adherent

Table 2 lists other typical data for a reverse current of $+0.05\,A\,cm^{-2}$ and a progressive increase of the pulse amplitude. In all the cases the deposits were compact and the current efficiency acceptable.

For all experiments the amount of charge was $162\,C\,cm^{-2}$ which is a typical value for batteries. It corresponds to $0.045\,A\,cm^{-2}$ for 1 h.

Table 3 lists data for the influence of the T_p/T_r ratio. This ratio is of interest when it is considered that the loading time for an electrical vehicle has to be short and as efficient as possible. Very good results were obtained with a 1/10 ratio for several pulse durations. Increasing the pulse duration too much led to the same damage as for direct current with a too high density, resulting in the appearance of dendrites. The frequency of the pulses was shown to be acceptable from 0.1 to 1 H3. A large number of experiments was performed with a typical value 0.3/3.

The observation of the pulse current clearly revealed how the zincate concentration was disturbed during the preceding rest time. For example, Fig. 6 shows the effect of a rest time which was too short between two consecutive pulses. In addition Fig. 7 shows how the sign of the flowing current during the rest time influenced the current during the next pulse. It was obvious that the best behaviour was achieved when the current pulse decreased only slightly, indicating that there was no limitation by lack of zincate in the diffusion layer.

Other important points are the parameters to be used relative to the zincate concentration. From several series of experiments we have summarized in Table 4 the upper and lower values to be used for the current densities during the pulse and rest times, in order to obtain a compact, adherent and non dendritic deposit.

Typical electron micrographs are shown in Fig. 8 and in which small, well-formed crystals may be noticed with a thickness of about 4 to 5 μm and a diameter of about 15 to 25 μm. When dendritic deposits were observed the main difference arose from the size of some crystallites which were made of an aggregation of very fine crystals. Figure 9 shows a micrograph for this special case.

The use of some additive compounds has been suggested previously for the avoidance of dendritic growth. Inorganic cations such as Pb^{2+} and Bi^{3+} have been used at low concentration, i.e. 10^{-4} M [1–2]. Organic compounds have also been added to 8 M KOH, such as fluorinated hydrocarbons [15] or polyethylenepolyamide [14]. In the present paper we have performed experiments with In^{3+}, Sb^{2+}, Tl^{+}, Pd^{2+}, Sn^{2+}, Pb^{2+} and Bi^{3+}.

Using the best conditions for a compact deposit it

Table 4. Average value of the parameters J_{max}, J_{min}, T_{pulse} and T_{rest} leading to a compact deposit recorded for three ZnO concentrations.

[ZnO] (M)	0.27	0.54	1.06
T_p (s)	<2	<2	<2
$R = T_p/T_r$	$0.06 < R < 0.075$	$0.06 < R < 0.085$	$0.06 < R < 0.1$
J_{max} ($A\,cm^{-2}$)	$J < 1.54$	$J < 2$	$J > 1.27$
J_{min} ($mA\,cm^{-2}$)	$J < 50$	$J > 25$	$J > 50$

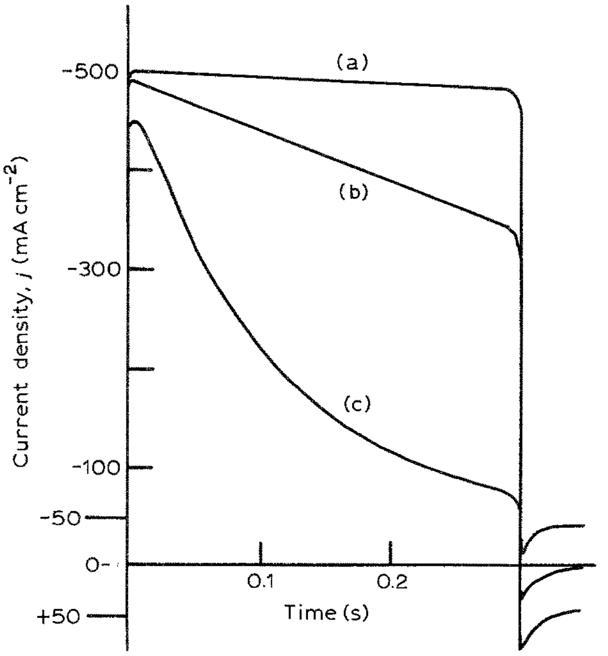

Fig. 7. Influence of the sign of the current density during the rest time. ($T_r = 3$s in this set of experiments): (a) $+50\,\mathrm{mA\,cm^{-2}}$, (b) $0\,\mathrm{mA\,cm^{-2}}$, and (c) $-50\,\mathrm{mA\,cm^{-2}}$.

was shown that both In^{3+} and Sb^{2+} led to more dendrites than if no additive were present, Tl^{+} and Pd^{2+} inhibited dendrites, but because of its high toxicity Tl^{+} was not investigated further nor was Pd^{2+} because of its price. With 10^{-4} M Pb^{2+} or Bi^{3+} the dendrites were strongly inhibited even when the current density was greater than the boundary values given in Fig. 2. Thus in Fig. 10, using a current density of $-75\,\mathrm{mA\,cm^{-2}}$ it is seen that lead and bismuth increased the compactness and stabilized the current better than if no additives were added.

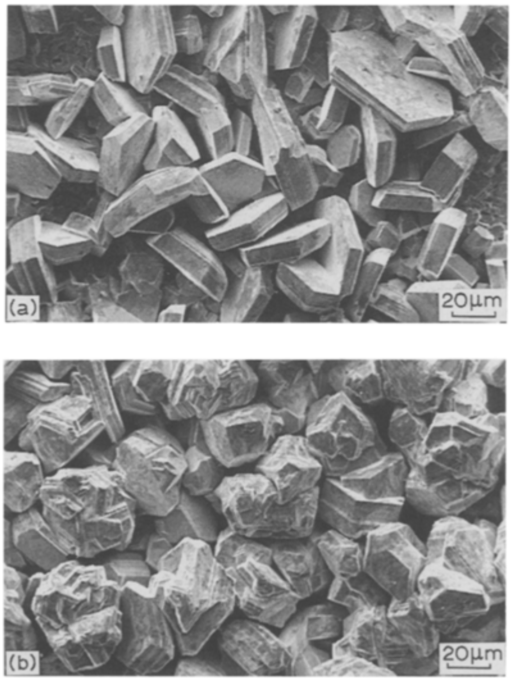

Fig. 8. SEM micrographs of the zinc deposits with pulsed currents. $j_{max} = -1\,\mathrm{A\,cm^{-2}}$ and $j_{min} = +0.05\,\mathrm{A\,cm^{-2}}$. (a) $T_p = 0.3$ s and $T_r = 3$s, (b) $T_p = 0.3$ s and $T_r = 4$s.

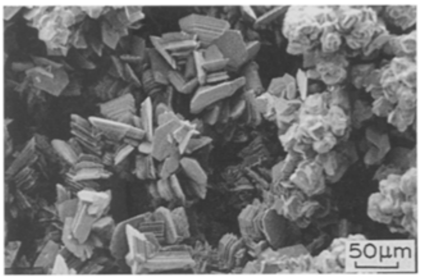

Fig. 9. SEM micrograph of the zinc deposit with pulsed current when the current is negative during the rest time. ($T_p = 0.3$ s and $T_r = 3$ s) $j_{max} = -1\,\mathrm{A\,cm^{-2}}$ and $j_{min} = -0.05\,\mathrm{A\,cm^{-2}}$.

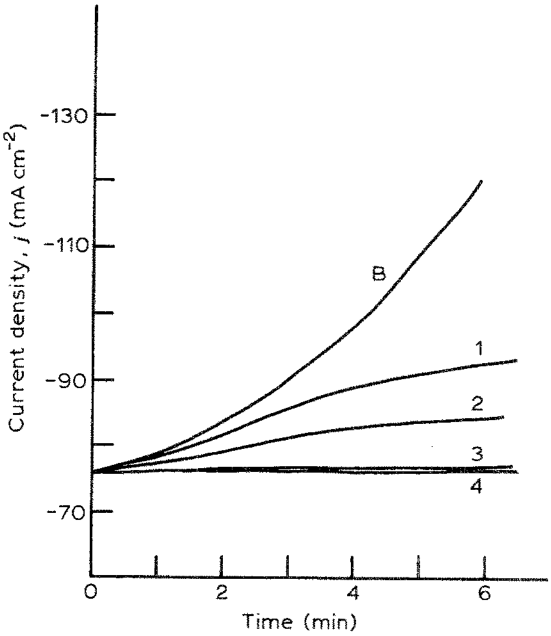

Fig. 10. Variation of the current density when bismuth or lead are choosen as additives to prevent dendrites. ($j_i = -75\,\mathrm{mA\,cm^{-2}}$) B: blank. [$Bi^{3+}$]: (1) 10^{-5}, (2) 10^{-4}, (3) 10^{-3} M [Pb^{2+}]: (4) 10^{-3} M.

Figure 11 shows that with lead small nodules composed of numerous very fine crystals appeared at the zinc surface, with a good adherence. The case of bismuth was nearly identical although with perhaps less zinc nodules although still with very fine crystals.

Several organic compounds were also tested, but unfortunatley only a few were able to inhibit dendrites. Sodium dodecylsulphate, cetyl-trimethylamine bromide and thiourea were unsuccessful additives. Glucose and starch were also tried and led to

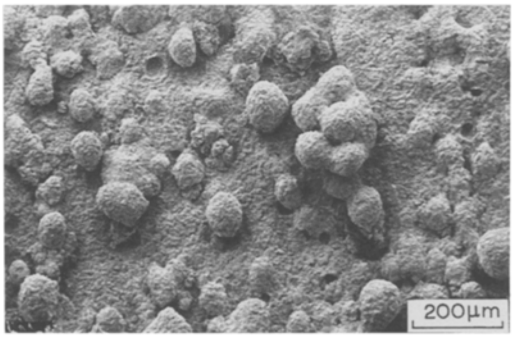

Fig. 11. SEM micrograph of zinc deposit obtained with a direct current density of $-54\,\mathrm{mA\,cm^{-2}}$ when 10^{-3} M Pb^{2+} is added.

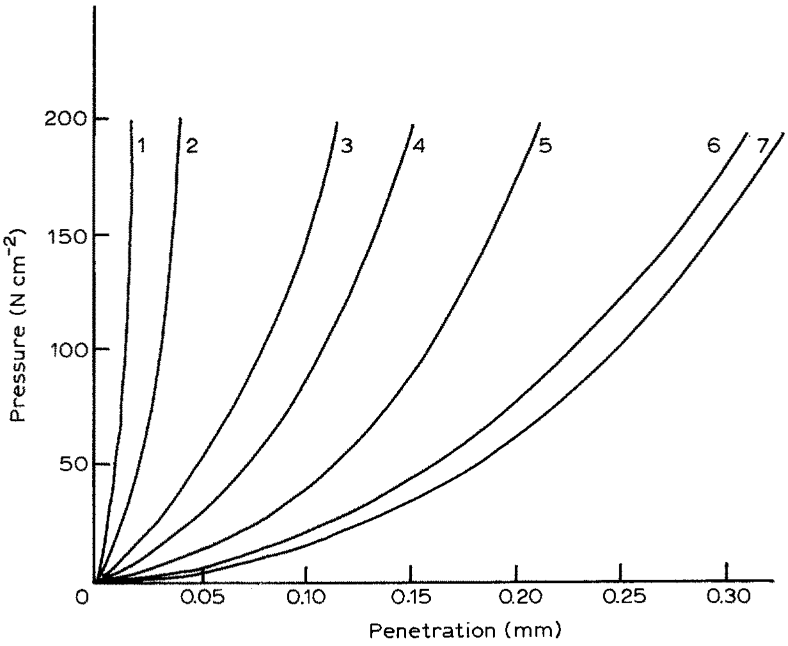

Fig. 12. Compactness measurements expressed by the penetration of a steel cylinder with a 0.1963 cm^2 section area prepared tool. (1) initial zinc plate, (2) d.c. deposit under stirring. $j = -45\,\mathrm{mA\,cm^{-2}}$, (3) deposit with pulsed currents. $T_p = 0.3$ s, $T_r = 3$ s, (4) d.c. deposit with 10^{-3} M of Bi^{3+} or Tl^+, (5) d.c. deposit with 10^{-3} M of Pb^{2+}, (6) d.c. deposit with 10^{-3} M of glucose, starch or FORAFAC 1110, (7) d.c. deposit with $j = -45\,\mathrm{mA\,cm^{-2}}$ without any stirring.

compact deposits. But a progressive oxidation of these compounds was noticed close to the counter electrode and the medium turned progressively brown.

In order to measure accurately the hardness of the deposits we designed a small stainless tool with a circular cross-section of 0.1963 cm^2. This was applied vertically on the horizontal zinc plate and the penetration length was recorded, in relation to the pressure. See Fig. 12. The best result was that of the initial zinc plate. The direct current deposit gave the poorest result, even when obtained with a suitable current density of $-45\,\mathrm{mA\,cm^{-2}}$. Stirred solutions were shown to promote a compact deposit with a hardness close to that of the zinc plate. For pulsed currents and additives such as lead or bismuth the compactness was a little less than above but was still acceptable. With the organic molecules such as starch, glucose and the Forafac surfactants, the deposits were compact, but it was obvious that this compactness was less great than that obtained using inorganic additives.

Multicycles of charge and discharge were performed in 8 M KOH with 1.08 M ZnO and a sufficient volume of electrolyte so that the decrease of the ZnO concentration during the charging step was negligible. Charge was obtained using the following parameters: $T_p = 0.3$ s; $T_r = 3$ s; $J_{max} = -1\,\mathrm{A\,cm^{-2}}$; $J_{min} = +0.05\,\mathrm{A\,cm^{-2}}$ for 1 h, and with a total charge of 163.6 C. The discharge time was 16 min with a direct current density of $45\,\mathrm{mA\,cm^{-2}}$. The counter electrode was a large scale (about 10 cm^2) zinc plate or carbon rod. Typically, more than 40 cycles were run without any dendritic growth. But it was observed that in unstirred solutions, the effects of the variations of the elecrolyte density led to a progressive change in the electrode geometry. Because of the higher density of the concentrated zincate solution, the deposit became thicker at the bottom of the zinc plate, and at the top, at the zinc air interface became progressively thinner. This observation was discussed earlier [1]. Even when a Teflon tape was firmly rolled around the zinc plate at the interface, as shown in Fig. 13, the same effect was observed, starting just at the limit of the Teflon tape on the immersed part. This observation confirmed the effect of the solution density and rule out the possible role of oxygen. If the same experiment was performed with a direct current during the charge time, the effect was more perceptible than with pulsed currents but when vigorous stirring was applied to the solution, the effect was negligible using direct or pulsed currents.

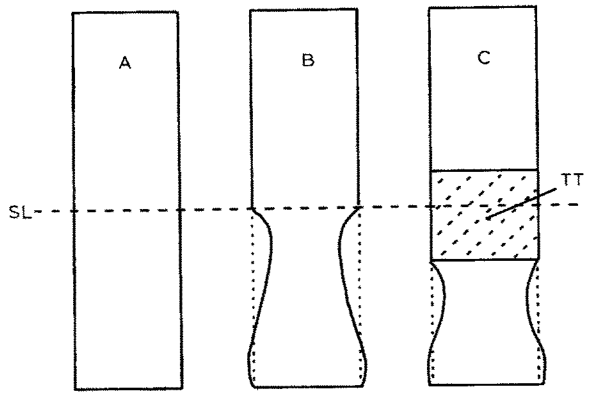

Fig. 13. Variation of the shape of the zinc electrode after 160 cycles. (A) initial, (B) with unprotected air-solution interface, (C) with a teflon tape as interface protector.

4. Conclusion

From the experiments reported here, it may be concluded that pulsed currents are particularly suitable in order to obtain a non dendritic deposit of zinc from a concentrated zincate solution in 8 M KOH. A 1 : 10 ratio for pulse and rest times is shown to be favourable in obtaining a deposit with an appreciable hardness and compactness, as well as a small anodic current during the rest time. Electronic microscopy has revealed that the additives greatly influence the morphology and the compactness of the zinc deposit.

Nevertheless care in the selection of the parameters mentioned above is required, with regard to the zincate concentration.

Acknowledgements

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