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The electrodeposition of zinc from acidified zinc sulphate solution

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In the electrodeposition of zinc from acidified zinc sulphate solutions the loss in current efficiency (CE) due to evolution of hydrogen at the cathode has often been attributed to the presence of metal impurities, and it has been thought that in a pure solution the CE would be 100%. In this paper it is argued that, whatever the degree of purity achieved, hydrogen must always be produced simultaneously with zinc. At the start of electrolysis the CE is determined solely by the zinc/acid ratio, but when impurities are present the CE falls progressively as electrodeposition proceeds. Further, colloid silica which is always present in plant solutions is not responsible for the CE falling below 100%, nor are the lead anodes that are used in practice. Some effects of manganese, both at the anode and the cathode, are reported. The deleterious influences of cobalt and manganese together are also discussed.

1. Introduction

In 1964 a relationship between the current efficiency and the composition of the solution was formulated [1], for the electrolytic zinc process

$$\frac{\text{zinc deposited}}{\text{hydrogen formed}} = \frac{1}{k}\,\frac{\text{zinc sulphate concentration}}{\text{sulphuric acid concentration}}.$$

This was a semi-empirical or intuitive relationship based on experimental work with the highly purified solutions to be described later.*

G. C. Bratt [2] has provided a theoretical basis for this relationship, which he calls 'Wark's Rule'. Bratt states that a similar relationship has been found to hold for co-deposition of nickel and hydrogen [3], which strengthens the case for its acceptance.

The value of k was almost independent of temperature, current density, and deposition period within the probable limits of operations for a commercial plant. Current efficiency (CE) for the experimental conditions most used by us† was 97·3 ± 0·3%; thus, about 2·5% of the current produced hydrogen.

It has been widely thought that the results from still more highly purified solutions might not conform to this equation, and indeed that current efficiencies would then be substantially higher until finally, with spectroscopic purity, only zinc would be produced. Tainton [4] was the first to advance this view; it has never been explicitly refuted.

The main purpose of the present paper is to demonstrate that, although experimental work with more highly refined solutions is certainly warranted, there is a considerable body of evidence from several hundred experiments that for the conditions mentioned above the current efficiencies can never exceed the values shown in Table 1. They may, however, approach them more closely in operating plants as control measures improve.

Table 1, which is taken from [1], indicates the

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* The research on which this relationship was based was conducted during 1926–29 for the Electrolytic Zinc Company of Australasia under the general direction of Sir David Orme Masson, with E. E. Jones as co-worker for a few months, and then with H. P. Matthews as collaborator. Company policy precluded publication at the time, but subsequently permission to publish certain aspects has been granted. The present paper is based on the experimental work of Matthews and the author.

† These were: temperature 35° C; current density 92 mA cm^{-2}; duration of deposition 1 h; [$ZnSO_4$] = 0·9 M, [H_2SO_4] = 0·6 M. The experimental technique was described earlier [1].

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Table 1. Current efficiency versus acidity

$ZnSO_4/H_2SO_4$ (*molecular ratio*)	*CE calculated* ($k = 30$)	*CE found*	
		1·5 M total sulphate	*2·125 M total sulphate*
5	99·3	99·2	98·9
2	98·3	98·2	98·0
1	96·8	96·4	96·5
0·5	93·7	93·0	93·3
0·2	85·7	85·2	85·8
0·09	73·2	(70)	

degree of reliability of the Wark Rule and emphasizes that the current efficiency is dependent primarily on the zinc sulphate/sulphuric acid ratio.

2. Experimental

The solutions used, possibly the purest ever obtained in quantity, were prepared by E. E. Jones who followed in general the purification steps then used in the commercial plant. Electrolytic zinc was dissolved in C.P. contact sulphuric acid. The solution was heated with excess zinc dust for self purification; basic zinc sulphates form during this treatment and these and/or zinc hydroxide, in separating out, remove iron, arsenic, etc. The solution was filtered hot. Addition of silver sulphate, followed by filtration, removed chloride. Cobalt was removed by the arsenic purification process, namely treatment of the hot solution with zinc dust in the presence of copper sulphate and sodium arsenite, followed by filtration. The filtrate was zinc dust purified to remove possible traces of arsenic, copper and cadmium. The final 'highly purified solution' was obtained by filtration of this solution after cooling to 25° C and air agitation; a considerable amount of basic zinc sulphate is removed during this treatment, and iron in solution is reduced to a very low concentration.

3. Results and discussion

The assays, taken from the earlier paper [1], are reproduced in Table 2; they show, in addition to minor traces of metallic elements, a significant concentration of silica, to which reference is made later. They also indicate a low concentration of dissolved basic sulphate which would be converted to the normal salt by the acid condition of the electrolytic cell.

It is pertinent to enquire whether these small amounts of metallic impurities or perhaps some unidentified impurity could have been responsible for the failure to obtain current efficiencies of 100% in the results reported in Table 1.

It would appear that any suspect impurity would, like cobalt, be deposited progressively on the zinc cathode. Its concentration in the solution would therefore decrease with time. As a consequence, if the electrolyte (with adjustment for concentration changes) were used with a fresh cathode for a second and a third time, increases in current efficiency could be expected. No such effects were ever observed in the work under discussion. The bulk solutions were used repeatedly without improvement or deterioration, as Table 3 shows in two instances (tests 87 and 88, and tests 89 and 90).

Table 2. Stock solutions of zinc sulphate

Component	*First batch* (mg l^{-1})	*Second batch* (mg l^{-1})
Zn	9·77 × 10^4	1·012 × 10^5
Mn	0·5 0·6	0·6
Co	nil	< 0·1
Cu	< 0·02	< 0·05
Cd	possible trace	< 0·2
Ni	nil	< 0·2
Fe	nil	< 0·1
Cl	trace	< 0·5
As	< 0·02	< 0·1
Sb	< 0·02	< 0·05
Pb	< 0·2	< 0·6
Al	–	< 0·5
SiO_2	15	15
SO_4	1·430 × 10^5	1·489 × 10^5

Table 3. Influence of current density on electrodeposition of zinc ($ZnSO_4$ = 0·9 M; H_2SO_4 = 0·6 M; 35° C; duration 1 h)

Test number	*Cathode potential** (V)	*Anode potential** (V)	*Nature of cathode*	*Solution*	*Cathode current density* (mA cm^{-2})	*Current efficiency* (%)	*Current efficiency corrected for re-solution* (%)
87	1·058–1·066	1·860–1·859	standard	fresh	92	97·6	97·7
88	1·056–1·064	1·856–1·853	from 87	from 87	86	97·6	97·7
28	1·053	–	standard	fresh	31·8	97·4	97·7
31	1·050	1·814	standard	fresh	31·8	97·4	97·7
89	1·048	1·754	standard	fresh	9·5	96·9	97·9
90	1·050	1·758	from 89	from 89	9·3	96·1	97·2
95	1·043	1·691	from 88	fresh	2·9	90·5	(94.4)?
96	1·046	1·648	from 95	fresh	0·95	87·0	97·8
	0·987	1·45–1·37	from 96	from 96	open circuit	4·4 mg loss in 1 h	

* Against saturated calomel electrode at room temperature (21° C ± 3° C).

It is well known in the industry that higher concentrations of impurities can be tolerated with higher current densities. In fact the Tainton version of the process was partly based on this fact. Therefore, had the value of less than 100% CE of our 'pure' solutions been due to the presence of unidentified metal impurities a substantial increase in current density should have raised the current efficiency. While there was some slight improvement with current density, it is significant (see Table 3) that a maximum value of CE had been reached at a relatively low current density.

There was some corrosion of cathode zinc deposits when they were left on open circuit for an hour in the electrolyte. The cathodic reactions associated with the corrosion could be hydrogen evolution or the reduction of an impurity (probably dissolved oxygen). If the current efficiencies (Table 3) are corrected for the dissolution of zinc in open circuit, there appears to be little effect of current density on current efficiency. The magnitude of the corrosion is of the order to be expected for the diffusion-controlled reduction of dissolved oxygen.

Still more conclusive evidence came from tests [1] when cobalt sulphate was added deliberately to the stock electrolyte. Cobalt did have a delayed disastrous effect on current efficiency, but there was no increased hydrogen evolution at the commencement of electrolysis, as the curves of paper [1] show conclusively. It appears, therefore, that cobalt could not have been responsible for the failure of electrodeposition to yield 100% current efficiencies.

3.1. *Effect of manganese*

Current plant-purification procedures do not remove manganese from the feed solutions, which contain several grams of manganese per litre. Plant operators are well aware that simultaneously with oxygen evolution manganese ions may be oxidized at the anode, either to permanganate and other manganates or to a more or less adherent layer of oxide on the lead anodes. There is also a possibility of alternating oxidation at the anode and reduction at the cathode with loss of electrical efficiency.

With up to 20 g^{-1} Mn it was found that, as for cobalt, the current efficiency is not initially diminished. However, the efficiency deteriorates substantially over a period of hours: simultaneously the permanganate colour may develop, and small particles of oxide, becoming detached from the anode, become suspended in the solution and may settle on the cathode. An attempt was made to determine the cause of the loss, which might have been due to (a) deleterious changes in the ionic state of the manganese similar to those for cobalt [1], (b) deterioration of the cathode due to

Table 4. Influence of additions of manganese from various sources or of MnO_2 (tests of 6 h duration)

Mn form and source	*CE test number*	*Initial Mn* (g l^{-1})	*Final Mn* (g l^{-1})	*Mean H_2SO_4* (M)	*Mean $ZnSO_4$* (M)	*CE* (%)	*Anode potential* (V)	*Mean temperature* (°C)	*Cathode current density* (mA cm^{-2})
no Mn	125	nil	nil	0·61	0·88	97·0	(1·815)*	34·95	29·3
$MnSO_4$, Hopkin and Williams	126	20·0	19·0	0·61	0·89	93·6	1·82	34·95	29·6
$MnSO_4$, Merck	127	20·0	19·6	0·61	0·89	94·2	1·83	34·95	29·1
$MnSO_4$, from Merck $KMnO_4$	135	18·7	18·2	0·61	0·88	93·4	1·80	35·05	29·7
added 0·6 g MnO_2 from Hopkin and Williams†	128	nil	nil	0·61	0·89	93·1	1·78	35·0	30·0
added 2·0 g MnO_2 from Merck $KMnO_4$ ‡	131, 2, 3	nil	nil	0·61	0·89	91·7	1·78	35·0	29·6

* The usual value for these anodes is rather lower [cf. 1·78 V in test 128 (without $MnSO_4$)]

† This MnO_2 was collected from tests 114 and 126

‡ Mean of three consecutive tests over 1–4 h.

Table 5. Influence of manganese on electrodeposition of zinc (1 h tests)

Mn concentration ($g\ l^{-1}$)	*CE test number*	*CE* (%)	*Cathode potential** (V)	*Anode potential** (V)	*Mean temperature*	*Cathode current density* ($mA\ cm^{-2}$)	*Cathode*	*Solution*	*Final Mn concentration* ($g\ l^{-1}$)	*Final acidity at 35° C*
0	107	97·5	1·046	1·804	35·0	31·8	fresh	fresh	—	0·63 M
	108†	96·8	1·042	1·795	34·85	31·2	from 107	from 107	—	0·68 M
5	110	97·0	1·046	1·63–1·89	35·1	30·2	fresh	fresh	4·56	—
	111†	97·1	1·050	1·63–1·79	35·0	29·4	from 110	from 110 filtered	4·41	0·65 M
20	112	97·4	1·054	1·66–1·76	35·0	29·1	fresh	fresh	19·1	0·63 M
	113†	96·9	1·054	1·69–1·80	35·0	29·6	from 112	from 112 filtered	18·8	0·64 M

* Against saturated calomel electrode at room temperature.

† These tests were second 1 h tests with cathode and solution from the preceding test.

Table 6. Effect of manganese; deterioration with time

CE test number	*CE* (%)	*Anode potential* (V)	*Mean temperature*	*Duration* (h)	*Solution*	*Cathode*
128	93·1	1·783	35·0	6	fresh	fresh
129	91·9	1·785	35·0	1	from 128	fresh
130	96·5	1·787	35·05	1	from 129 filtered	fresh

adhering oxide particles, or (c) alternate oxidation to manganate or manganese (III) at the anode and reduction to manganese (II) ions at the cathode. To determine the significance of the last-mentioned possibility the technique of Buttinelli and Iacchelli [5] could be employed, namely to measure the amount of hydrogen produced at the cathode. If this, added to the zinc produced, falls short of 100% in current efficiency then changes in the ionic condition of the manganese must be held responsible. Another useful technique would be to use a two-component electrolysis cell [1], determining the manganate concentrations in both anolyte and catholyte compartments. Deposition of manganese metal with the zinc must be ruled out because of the very low manganese content in zinc cathodes.

Care was taken to ensure that troublesome impurities were not introduced with the manganese. Three different samples, one starting from permanganate, were prepared. Table 4 shows that over a period of 6 h they behaved similarly. It also proves that manganese dioxide in suspension, even in the absence of dissolved manganese, caused serious losses.

In Table 5 the results for two different concentrations of manganese are compared with the quite normal results for pure solutions (tests 107 and 108). For these tests of short duration the manganese had little or no effect, whereas with the 6 h periods of Table 4 current efficiencies were already seriously reduced. The electrolyte from test 128 of Table 4 containing only suspended MnO_2, when used with a fresh cathode in test 129, gave a current efficiency in a 1 h test of only 91·9%. Comparing this with the results of Table 5 it is apparent that any inroads on CE are made by the oxidation products of manganese rather than dissolved manganous ion.

The influence of suspended MnO_2 is further confirmed by the fact that after filtration the solution from test 129 recovered to give a current efficiency of 96·5% (see Table 6).

There is little or no permanent deterioration in the cathodically deposited zinc from prior contact with manganese oxide, as is shown in Table 7.

In plant practice glue is usually added to minimize the loss in current efficiency due to undesirable impurities. Its marked influence for cobalt-bearing solutions has been reported [1]: glue delayed but did not prevent a fast-accelerating deterioration in CE. A similar situation arises for manganese, as is shown in Table 8: the lower than normal current efficiencies were due to use of a higher acid concentration. Because of the manganese dioxide carried by the electrolyte the current efficiencies cannot be duplicated with the same precision as in 'pure' solutions or in solutions containing cobalt as the only added impurity.

Cathode potentials (routine measurements

Table 7. Cathode or solution effect

CE test number	*Mean Mn* ($g l^{-1}$)	*Cathode*	*Solution*	*CE* (%)	*Anode potential* (V)	*Mean acid at 35° C*
119	18·5	*seventh hour's use*		94·3	–	0·64 M
120	18·6	fresh	from 119	94·0	1·83	0·64 M
121	nil	from 119	fresh 'pure'	97·1	1·84	0·61 M

Table 8. Effect of glue in restraining manganese in electrodeposition of zinc

Test number	*Glue*	*Mn (dissolved)* (g l^{-1})	*CE* (%)	*Cathode potential* (V)	*Anode potential* (V)*		*Duration of test* (h)	*Deposit*
					Left	*Right*		
291	nil	nil	96·5	1·038	1·85–1·83	1·85–1·83	24	a small number of nodules had begun to form; shining surface.
295	5 mg l^{-1} + 1 mg h^{-1}	nil	96·3	1·047	1·84–1·82	1·84–1·82	24	typical smooth deposit with a few nodules; duller than test 291.
296	nil	2·0–1·93	75·1	1·033	1·73–1·75	1·82–1·83	15	marked edge growths and nodules; dull and even; few holes.
288†	5 mg l^{-1} + 1 mg h^{-1}	2·0–1·63	88·0	1·044	2·39–1·84	2·46–1·97	24	very highly vegetated at the edge and even in the centre; would give very low melting efficiency.

* The cathode was placed centrally between two anodes, referred to here as left and right.

† The high anode potential of test 288 was due to the anodes having stood out of action for some time prior to the test.

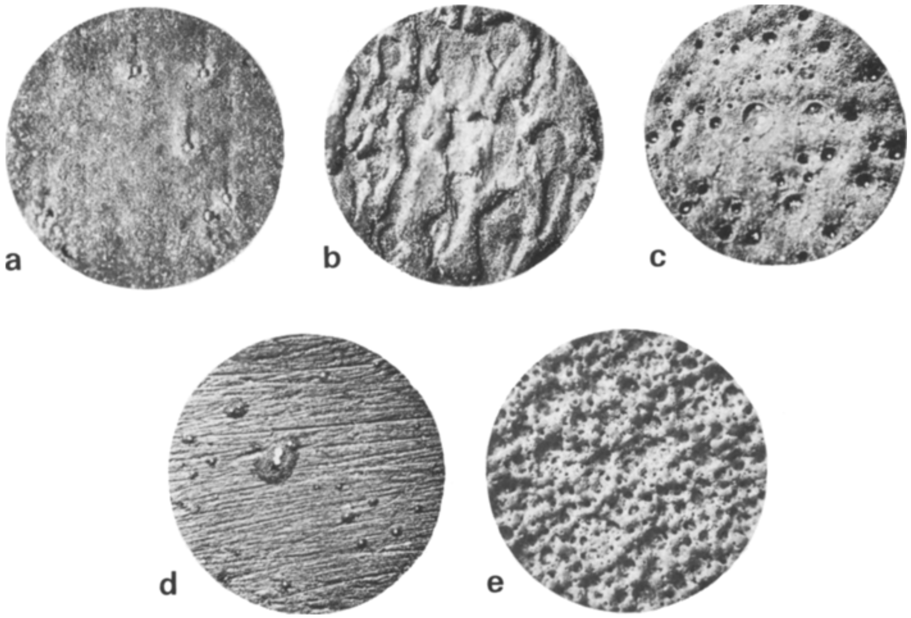

Fig. 1. (a) Zinc deposit from highly purified solution: rising hydrogen bubbles have caused the striations; (b) fine-grained deposit from highly purified solution to which glue has been added; (c) front and (d) reverse views of zinc from cobalt-bearing solution; the striations of the reverse side are due to use of a roughened aluminium anode; note that corrosion has already commenced in the typical 'cobalt holes'; (e) typical deposit from a manganese-bearing solution (× 7·2)

against the saturated calomel electrode) are reported for this series of tests because they show that glue, which improved current efficiency, may slightly reduce energy efficiency by raising the cell voltage. The final column reports on the condition of the deposited zinc which was markedly dependent on the solution composition and the particular impurities present. All our deposits were examined microscopically, and Fig. 1 shows characteristic photographs for some experimental conditions. Each element has a characteristic effect on the morphology of the deposit, but it is not always possible to identify it by examining deposits formed in the complex solutions of practice. Antimony in sufficient amounts gives rise to a cauliflower effect, selenium to a smooth deposit to which hydrogen bubbles adhere and glide slowly upwards.

3.2. *Anode effects in the presence of manganese and cobalt*

When cobalt and manganese were both introduced the results could not be quantitatively predicted from the results for each separately. Dominating factors were the prior history of the lead anodes and the condition of the anode scale. Routine measurements of the anode potential, accurate to 1 mV, were found to vary little during the progress of electrodeposition for any test within the whole series except when manganese was present. (Lead anodes tend to become passive when not in continuous use, sometimes to the extent of several volts of overvoltage. They return gradually to normal after a few days, and in the meantime in pure solution have negligible effect on current efficiency.) In the presence of manganese the establishment of relatively stable conditions is slow. The solution may become clouded with suspensions of varying degrees of fineness; it may develop the permanganate colour; sizeable chips of oxide may break away from the anode. These chips may contain some cobalt oxide; at any rate the two elements together can be much more harmful than either alone. Once again the current efficiency of the first few minutes is unaffected.

Table 9 records the results from a typical series of tests of 5 h duration, indicating how toxic cobalt can be with anodes from solutions containing both cobalt and manganese, and also how important is voluntary or involuntary disturbance of the MnO_2 deposit.

The high CE (96·7%) of the 5 h test 285, with a pure solution but with anodes aged in an electrolyte containing both cobalt and manganese, illustrates that the current efficiency of zinc deposition is at first unaffected by the condition of the anodes. Later as the impurities passed into solution or suspension, a marked loss would have occurred. The anodes themselves require several days to

Table 9. Influence of anode condition on current efficiency and nature of deposit (tests of 5 h duration)

Test number	*Anodes*	*Solution*	*Mn elimination, first 2 h* ($g\ l^{-1}\ h^{-1}$)	*CE* (%)	*Zinc deposit*
285	with heavy scale from Co–Mn solution	standard zinc and acid concentrations, Co and Mn-free	–	96·7	no visible 'Co holes'
286	aged in manganese-free cobalt-bearing solution	standard plus 100 mg l^{-1} Co, Mn-free	–	89·8	minor cobalt re-solution holes
281	aged and scaled in Co–Mn solution	as for 286 plus 2 g l^{-1} Mn	0·035	52·0	heavy re-solution
282	as for 281	as for 286 plus 5 g l^{-1} Mn	0·17	62·3	heavy re-solution
283	from 281, scale scraped	as for 286	–	53·2	heavy re-solution
284	from 282, heavy scale	as for 286	–	70·2	heavy re-solution

attain a steady condition in manganese-bearing solutions, a fact noted also by Buttinelli and Iacchelli [5].

While discussing the influence of the condition of lead and lead-coated anodes it is pertinent to ask whether the current efficiencies lower than 100% could have been caused by their use. It was found, however, that substitution for them of platinum black anodes left the current efficiencies practically unaffected.

3.3. *Effect of silica*

Table 2 showed that the 'pure' solutions used contained 15 mg l^{-1} SiO_2, presumably in colloid form derived from the ore and the glass vessels used. In commercial plants the concentration may reach 100 mg l^{-1}. It is well known that some colloids exert a restraining influence on such impurities as cobalt (see for example [6, 7]). Thus, the silica in these solutions may have raised (but surely not lowered) current efficiency. A comparison was made between the stock solution and another prepared from highly purified zinc sulphate crystals and sulphuric acid, containing only 2 mg l^{-1} SiO_2. A higher than usual acid/zinc ratio led to lower current efficiencies than normal, but in agreement with Table 1.

While 15 mg l^{-1} SiO_2 had no more influence on the current efficiencies of pure solutions than 2 mg l^{-1}, silica has a marked effect in reducing the ravages of cobalt and manganese. Table 10 compares the effects of sodium silicate, zinc silicate and glue on a solution containing 20 mg l^{-1} Co and 2 g l^{-1} Mn that had previously been rendered toxic by prolonged electrolysis.

The zinc salt seems, on this limited series of tests, to be a better restraining agent than the sodium, but neither is as effective as glue. A conclusion to be drawn is that it is unlikely that the 15 mg l^{-1} SiO_2 in our pure solutions could have been responsible for their falling short of 100% in current efficiency.

One other possibility remains. It will be seen that during the purification sequence our two stock solutions were treated with zinc dust. It might therefore be suspected that they had carried forward some degree of the cobalt 'devilment' factor ([1], p. 897) into the electrolytic cell. However, test 52 of Table 11, for which the electrolyte had not been pre-treated in this manner, gave precisely the same result as test 34, which had.

Despite the passage of 50 years since the process was introduced, it was still so little understood in 1969 that a disastrous situation could arise at Risdon [8], where there were periods of

Table 10. Effect of silica on electrolysis of Co–Mn solutions

Test number	*Addition agent and amount*	*Duration* (h)	*CE* (%)
341	nil	5	78
340	glue, 10 mg l^{-1}	7	94·1
342	SiO_2, 20 mg l^{-1} as sodium salt	5	85·1
345	SiO_2, 100 mg l^{-1} as sodium salt	5	83·6
344	SiO_2, 1000 mg l^{-1} as sodium salt	5	89·7
351	SiO_2, 100 mg l^{-1} as zinc salt	5	88·3
346	SiO_2, 1000 mg l^{-1} as zinc salt	5	92·0

Table 11. Influence of dissolved silica on current efficiency ($ZnSO_4$ = 0·25 M; H_2SO_4 = 1·25 M; duration 1 h)

Test number	*Silica content* (mg l^{-1})	*Current efficiency* (%)	*Solution*
34	15	84·8	'pure' (bulk solution)
46	15	85·5	'pure' (bulk solution)
52	2	84·8	from $ZnSO_4$ crystals

'catastrophic unexplained collapses' in current efficiency. At times, more zinc was dissolving than was being deposited: the trouble was traced to nickel and chromium, and efficiencies then improved. A continuation of the type of work reported here seems desirable for such elements as nickel and chromium, and a reversion to X-ray analysis of the deposited zinc [1] as a means of early detection of obtruding impurities.

4. Conclusions

Summarizing, it is concluded that at the commencement of electroylsis the current efficiencies with respect to hydrogen and zinc deposition are determined solely by the acid/zinc ratio. With impurities present there is an increasing rate of hydrogen evolution as the deposition progresses, and this may be a result of hydrogen deposition on exposed foreign-metal aggregates.

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