

# Electrolytic Deposition of Zinc from Acid Solutions

By

Hisashi Kiyota

(Received July 18, 1932)

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There are a great many works dealing with electrolytic deposition of zinc from various acid solutions, but none of the methods hitherto proposed could be regarded as perfect. As the chief difficulty in zinc electrolysis was thought to lie in the specific property of zinc of forming a spongy deposit, an attempt was made, in this investigation, to ascertain how far this difficulty might be overcome by controlling the current density on the one hand and the concentration of acid on the other. It soon became clear that, in order to obtain reliable results, the current density must be restricted within certain limits which vary according to the concentration of acid. In an acetic acid solution the limits within which the current density must be restricted are comparatively wide, while in a sulphuric acid solution they are so narrow that exact working is hardly practicable.

The zinc sulphate used in the experiment was prepared either by dissolving pure zinc obtained from E. Merck in dilute sulphuric acid so as to make the concentration of free acid in the resulting zinc sulphate solution nearly  $1/10$  normal, or by first neutralizing the acid in the zinc sulphate solution with caustic soda and then adding an amount of acetic acid properly calculated to make its concentration in the solution  $1/10$  normal.

Throughout all the experiments a platinum basin was always employed as the cathode, and in order to know what kind of results would be attainable, when the methods previously known were worked with this cathode, a series of experiments was performed according to the

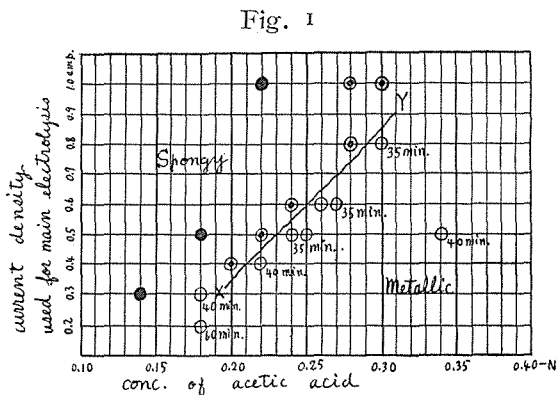
methods given by F. Spitzer<sup>1</sup>, A. Fischer and R. J. Boddaert<sup>2</sup>, F. F. Exner<sup>3</sup>, and L. H. Ingham<sup>4</sup>. None of these methods, however, gave satisfactory results, always producing the deposit in spongy forms, some of which were found to adhere to the cathode so loosely that even washing of it could not be effected.

A thorough revision of the electrolysis of zinc, which was thus deemed indispensable, was carried out by the present author, very minute attention being paid both to the current density for the electrolysis and to the concentration of acid in the zinc sulphate solution.

### A. Acetic Acid Solution

I. With a platinum basin of about 150 c.c. capacity previously plated with copper as the cathode, electrolysis was conducted by rotating the anode consisting of a platinum disk at the rate of about 1500 revs. per minute. As the electrolyte, a solution containing about 0.1 gram. of zinc, 6 grams. of crystalline sodium acetate, some sodium sulphate (below 0.02 normal) and different quantities of acetic acid in 125 c.c. was taken, and this was electrolysed by passing a current of comparatively small density (main electrolysis), till the electrolyte ceased to give the potassium ferrocyanide reaction for zinc and then raising the current density to about 3 amperes (final electrolysis) for about 10 minutes. The results are shown in Fig. 1.

Generally speaking, the region lying below the line XY gave the zinc deposit in a metallic form, while that lying above the line produced the spongy



1. F. Spitzer; Zeitschr. f. Elektrochem., **11** (1905), 404.
2. A. Fischer and R. J. Boddaert; Zeitschr. f. Elektrochem., **10** (1904), 946.
3. F. F. Exner; Journ. Am. Chem. Soc., **25** (1903), 899;  
Chemisches Zentralblatt, **2** (1903), 1210.
4. L. H. Ingham; Journ. Am. Chem. Soc., **26** (1904), 1270;  
Chemisches Zentralblatt, **2** (1904), 1758.

or powdery deposit. The cases in which zinc was electrolysed as a deposit with metallic lustre and bluish white colour are marked with  $\circ$ , and those, in which the results were tolerably good, only the last small portion of the deposit being produced in a spongy state, are marked  $\odot$ . The third mark  $\bullet$  stands for the worst cases which could, by no means, be used for analytical purposes. The time required for complete deposition was 35–60 minutes and is given in the figure under the mark  $\circ$ .

II. In the next series of experiments, the current density for the main electrolysis was kept at 0.5 ampere, and the concentration of acetic acid and the current density for the final electrolysis were changed. The results are shown in table I (No. 1—No. 18) and Fig. 2.

Table I

A

No.	ELECTROLYTE				
	Zn mgms.	Conc. of acetic acid (Normality)	$\text{CH}_3\text{CO}_2\text{Na}\cdot 3\text{H}_2\text{O}$ gms.	Conc. of $\text{Na}_2\text{SO}_4$ (Normality)	Volume c.c.
1	100.6	0.27	6	0.02	125
2	"	"	"	"	"
3	"	"	"	"	"
4	"	"	"	"	"
5	"	"	"	"	"
6	"	0.40	"	"	"
7	"	0.37	"	"	"
8	"	0.35	"	"	"
9	"	0.34	"	"	"
10	"	0.33	"	"	"
11	"	0.40	"	"	"
12	"	0.37	"	"	"
13	"	0.35	"	"	"
14	"	0.34	"	"	"
15	"	0.33	"	"	"
16	"	0.32	"	"	"
17	"	0.24	"	"	"
18	"	0.33	"	"	"

Table I

B

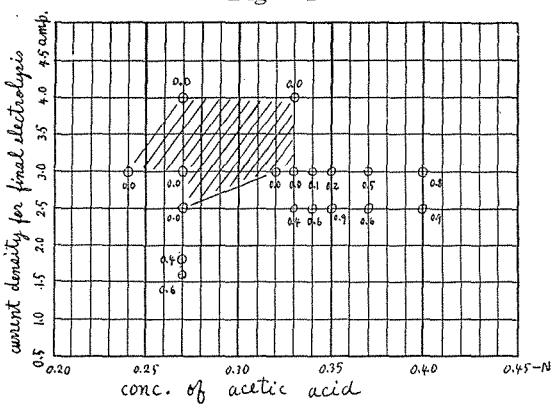
No.	Main Electrolysis				Final electrolysis (About 10 minutes)			Error mgms.
	Current density ND <sub>100</sub> amp.	Volts	Temp.	Time mins.	Current density ND <sub>100</sub> amp.	Volts	Final temp.	
1	0.5	6.1-6.0	16-24°	55	1.6	10.4- 8.8	38°	-0.6
2	"	6.2-6.2	17-24°	45	1.8	11.6-10.4	40°	-0.4
3	"	6.1-6.1	18-24°	"	3.0	15.6-13.4	53°	-0.0
4	"	6.2-6.1	15-23°	"	2.5	13.8-11.6	45°	-0.0
5	"	6.1-6.2	15-23°	"	4.0	19.6-15.4	73°	-0.0
6	"	6.2-6.0	14-24°	"	2.5	13.6-11.4	43°	-0.9
7	"	—	—	"	"	—	—	-0.6
8	"	—	—	"	"	—	—	-0.9
9	"	—	—	"	"	—	—	-0.6
10	"	6.2-6.1	17-23°	"	"	13.4-11.2	45°	-0.4
11	"	6.0-6.1	16-22°	40	3.0	16.2-13.0	52°	-0.8
12	"	—	—	45	"	—	—	-0.5
13	"	—	—	"	"	—	—	-0.2
14	"	—	—	40	"	—	—	-0.1
15	"	6.0-6.0	17-24°	45	"	16.6-13.2	54°	-0.0
16	"	—	—	"	"	—	—	-0.0
17	"	6.1-6.0	17-24°	"	"	16.4-13.2	57°	-0.0
18	"	6.1-6.1	17-23°	40	4.0	19.8-15.0	72°	-0.0

Fig. 2

In the region marked by oblique lines the zinc was found to be deposited quantitatively. The error, which was always negative, is given in the figure by numbers which represent milligrams.

Combining the results of the above two series of experi-

ments we may conclude that the best conditions for electrolyzing zinc from an acetic acid solution are as follows :



Concentration of acetic acid: 0.27-0.33 normal

Current density for main electrolysis: 0.5-0.6 ampere

„ „ „ final electrolysis: 3-4 amperes

III. In the foregoing two series of experiments the amount of zinc for each analysis was always about 0.1 gram. A third series of experiments was now undertaken to see how the electrolysis would be effected by the concentration of zinc in the electrolyte, and to learn how the concentration of the acid should be changed according to the amount of zinc. As will be seen from the results shown in Table II, the suitable normality of acid for electrolyzing 0.5 gram of zinc was found to be between 0.14 and 0.21. In a more diluted acid solution the zinc crystals became somewhat coarse. When the amount of zinc was 0.3 gram the best result was produced by maintaining the normality of acid at 0.21—0.27 normal. With a solution in which the amount of zinc present was as small as 0.001 gram in 125 c.c. the cathode should previously be plated with zinc, otherwise, not only is the current yield very much lowered, but complete deposition of zinc becomes unattainable. The results are shown in Table II.

Table II

A

No.	ELECTROLYTE				
	Zn mgms.	Conc. of acetic acid (Normality)	CH <sub>3</sub> CO <sub>2</sub> Na•3H <sub>2</sub> O gms.	Conc. of Na <sub>2</sub> SO <sub>4</sub> (Normality)	Volume c.c.
1	500.0	0.13	6	0.02	125
2	„	„	„	„	„
3	„	0.15	„	„	„
4	„	„	„	„	„
5	„	0.21	„	„	„
6	„	„	„	„	„
7	„	0.15	„	„	„
8	„	0.21	„	„	„
9	300.0	„	„	„	„
10	„	„	„	„	„
11	„	0.27	„	„	„
12	„	„	„	„	„
13	1.0	0.30	„	„	„
14	„	0.36	„	„	„
15	„	„	„	„	„

Table II  
B

No.	Main Electrolysis				Final Electrolysis (10 minutes)			Error mgms.
	Amp. (ND <sub>100</sub> )	Volts	Temp.	Time mins.	Amp. (ND <sub>10</sub> )	Volts	Final temp.	
1	0.5	—	—	80	3.0	—	—	+0.1
2	0.6	—	—	75	"	—	—	-0.0
3	0.5	—	—	75	"	—	—	-0.0
4	"	—	—	80	"	—	—	-0.0
5	"	5.7-5.7	17-24°	80	"	15.4-12.6	58°	+0.1
6	0.6	6.0-6.0	17-28°	65	"	16.0-11.4	55°	-0.1
7	0.5	5.8-5.9	17-27°	75	4.0	18.8-14.4	76°	+0.1
8	"	—	—	"	"	—	—	-0.0
9	0.6	6.3-6.3	16-23°	50	3.0	16.2-12.0	53°	+0.0
10	0.5	6.0-5.9	17-25°	60	4.0	20.0-14.6	73°	-0.0
11	"	—	—	70	3.0	—	—	-0.0
12	"	—	—	60	4.0	—	—	+0.1
13	"	—	—	0	3.0	17.8-12.6	52°	-0.0
14	"	6.1-6.1	18-25°	15	"	—	—	-0.1
15	"	—	—	0	3.5	—	—	-0.0

Table III  
A

No.	ELECTROLYTE				
	Zn mgms.	Conc. of acetic acid (Normality)	Acetate	Other Salts	Volume c.c.
1	500.0	0.15	CH <sub>3</sub> CO <sub>2</sub> Na•3H <sub>2</sub> O 6 gms.	Na <sub>2</sub> SO <sub>4</sub> 0.15-N	125
2	"	"	"	"	"
3	"	"	CH <sub>3</sub> CO <sub>2</sub> NH <sub>4</sub> 3.4 gms.	Na <sub>2</sub> SO <sub>4</sub> 0.02-N	"
4	100.6	0.33	CH <sub>3</sub> CO <sub>2</sub> Na•3H <sub>2</sub> O 6 gms.	NaNO <sub>3</sub> 0.03-N Na <sub>2</sub> SO <sub>4</sub> 0.02-N	"
5	"	"	"	NaNO <sub>3</sub> 0.1-N Na <sub>2</sub> SO <sub>4</sub> 0.02-N	"
6	"	"	"	NaCl 0.15-N Na <sub>2</sub> SO <sub>4</sub> 0.02-N	"
7	105.4	"	"	NaCl 0.03-N Na <sub>2</sub> SO <sub>4</sub> 0.02-N	"
8	"	"	"	"	"

Table III

B

No.	Main Electrolysis				Final Electrolysis (10 minutes)			Error mgms.
	Amp. (ND <sub>100</sub> )	Volts	Temp.	Time mins.	Amp. (ND <sub>100</sub> )	Volts	Final temp.	
1	0.6	6.0-6.0	17°-24°	70	3.0	14.4-11.2	48°	-0.0
2	0.5	—	—	85	„	14.2-10.2	50°	-0.1
3	„	5.7-5.5	19-25°	80	1.5	8.5- 8.1	34°	-0.5
4	„	5.3-5.7	18°-27°	110	3.0	14.8-11.6	53°	+0.1
5	„	—	—	300				
6	„	5.3-5.2	17°-24°	50	3.0	12.4-10.8	50°	-1.5
7	„	5.5-5.7	18°-26°	55	„	15.6-12.8	53°	-0.6
8	„	—	—	50	4.5	19.0-14.0	78°	-0.1

IV. The influence of such substances as sodium sulphate, ammonium sulphate, ammonium acetate, sodium chloride and sodium nitrate on zinc deposition was investigated and the results tabulated in Table III were obtained. The presence of sodium sulphate, ammonium sulphate and ammonium acetate has no significant bad influence, when their dilution is lower than 0.15 normal. Nitrates greatly retard deposition of the metal and tend to make the zinc deposit spongy. The effect of chlorides is not nearly so bad as that of nitrates, but still they often become a cause of negative error.

### B. Sulphuric Acid Solution

Electrolysis of a sulphuric acid solution containing about 0.1 gram of zinc, and from 0 to 18 grams of sodium acetate was carried out nearly in the same manner as in the electrolysis of the acetic acid solution. The current density for the main electrolysis was maintained between 0.4-0.5 ampere, and that for the final electrolysis at 3 amperes, and the electrolytic bath was cooled by a current of cold water.

So far as the present experiments are concerned, electrolytic deposition of zinc from a sulphuric acid solution could not be achieved with satisfactory results even by controlling the current density and the concentration of the acid in several ways. In Fig. 3 the results obtained by passing a current of 0.5 ampere for main electrolysis are shown. The cases in which comparatively good results were obtained are shown by the mark ○, while the mark ⊙ stands for those which

were not so good, and ● for the worst cases. It may thus be concluded that for zinc electrolysis in a sulphuric acid solution, the acidity of the bath, which must contain about 0.1 gram of zinc and 6 grams of sodium acetate in 125 c.c., should be kept between 0.14-

0.26 normal, and a current of 0.5 ampere should be passed for the main electrolysis.

Experiments were next conducted with the bath containing 5, 6 or 7 grams of sodium acetate, and a current of 0.4 ampere for the main electrolysis. In these cases too, the solution containing 6 grams of sodium acetate was found to give the best results if the concentration of sulphuric acid were kept at 0.18 normal, as is seen in Table IV and Fig. 4.

Table IV

A

No.	ELECTROLYTE			
	Zn mgms.	$\text{CH}_3\text{CO}_2\text{Na}\cdot 3\text{H}_2\text{O}$ gms.	Conc. of $\text{H}_2\text{SO}_4$ (Normality)	Volume c.c.
1	99.9	6	0.22	125
2	"	"	0.20	"
3	"	"	0.18	"
4	"	"	0.16	"
5	"	"	0.14	"
6	"	"	0.22	"
7	"	5	0.18	"
8	"	"	0.16	"
9	"	"	0.14	"
10	"	7	0.22	"

Fig. 3

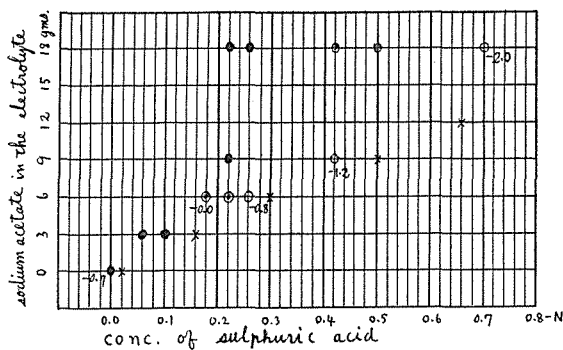


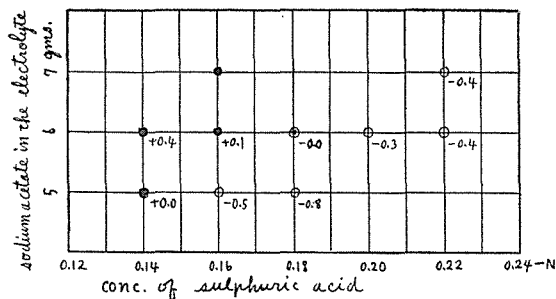


Table IV

B

No.	Main Electrolysis				Final Electrolysis (10 minutes)			Error mgms.
	Amp. (ND <sub>100</sub> )	Volts	Temp.	Time mins.	Amp. (ND <sub>100</sub> )	Volts	Final temp.	
1	0.4	5.3-5.2	15°-21°	45	3	15.4-15.2	29°	-0.4
2	"		15 -21°	"	"		25°	-0.3
3	"		14 -21°	55	"		29°	-0.0
4	"		18 -24°	85	"		28°	+0.1
5	"	5.2-5.2	17 -22°	55	"	15.6-15.2	26°	+0.4
6	"		16 -23°	60	3.5	18.4-17.8	28°	-0.4
7	"	5.4-5.3	17 -22°	45	3	16.8-16.4	26°	-0.8
8	"		17 -20°	60	"		28°	-0.5
9	"		17 -24°	"	"		27°	+0.0
10	"	5.0-5.0	18 -20°	45	"	15.2-14.8	28°	-0.4

Fig. 4



### Summary

1) All the methods hitherto proposed for electrolysing zinc from an acid solution were experimentally confirmed to give no satisfactory results, when a Classen's electrode is employed.

2) The best conditions necessary for producing zinc in a metallic form on Classen's electrode from an acid solution quantitatively were sought by controlling the current density on the one hand and the concentration of the acid on the other.

3) Though in the case of sulphuric acid solutions it was hardly possible to find any conditions under which zinc deposition could be worked with complete safety, a very satisfactory and reliable method was found with acetic acid solutions.

4) In carrying out the electrolysis, a current of 0.5-0.6 ampere should first be passed, till the solution ceases to give the potassium ferrocyanide reaction for zinc, and then the current density should be raised to 3-4 amperes for a further 10 minutes. The faster the anode is rotated the better is the deposit produced.

5) The concentration of acetic acid should be adjusted according to the amounts of zinc present in the following way:

For 0.5 gram Zn	0.15-0.21 normal
„ 0.3 „ „	0.21-0.27 „
„ 0.1 „ „	0.27-0.33 „

6) The duration of the electrolysis varies from 35 minutes to 80 minutes according to the amounts of zinc, thus—

0.5 gram Zn	65-80 min.
0.3 „ „	50-60 „
0.1 „ „	35-40 „

7) The presence of such salts as sodium sulphate and ammonium sulphate does not interfere with the electrolysis, if their concentration is below 0.15 normal. Nitrates and chlorides must not be present in the bath.

8) Under the conditions above stated the zinc deposit is obtained as a smooth metallic coating, so that the electrode thus coated may be used directly for the next electrolytic analysis of zinc.

The author takes this opportunity of expressing his warm thanks to Professor Motooki Matsui, under whose guidance and encouragement this work was carried out.

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