THE ELECTROLYTIC DEPOSITION OF ZINC FROM ACID SOLUTIONS.

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Received April 2nd, 1935. Published August 28th, 1935.

There have been a great many works dealing with the electrolytic deposition of zinc from the various acid solutions, but none of the methods hitherto proposed can be regarded as perfect. The chief difficulty in zinc electrolysis was thought to lie in a property of zinc, which forms a spongy deposit, and an attempt was made, in this investigation, to ascertain how far this difficulty might be overcome and to establish a convenient method for the quantitative analysis of zinc.

Throughout all the experiments, a platinum basin of about 150 c.c. capacity previously plated with copper was employed as the cathode, and a platinum disk which could be rotated as the anode.

In order to find out what results were attainable when the methods previously known were followed with this apparatus, a series of experiments was performed according to the methods given by F. Spitzer,(1) A. Fischer and R. J. Boddaert,(2) F. F. Exner,(3) and L. H. Ingham.(4) None of these methods, however, gave satisfactory results, all producing the deposit in spongy form, and some giving a deposit adhering to the cathode so loosely that even washing could not be effected.

The best results were obtained by the present author with an acetic acid solution containing some sodium acetate. An outline of the experiment follows.

The sample of zinc was taken below 0.5 g. from the analytical standpoint. The suitable volume of the electrolyte was found to be about 125 c.c. To see the effects of many important factors they were fixed in a range suitable for the analytical purpose and the electrolysis was carried out, changing at a time one factor only to be tested. The following results were obtained : (A) Zinc tended to deposit in a fine crystalline form with a metallic lustre giving a negative error in the cases where (1) the concentration of the acetic acid

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(1) F. Spitzer, *Z. Elektrochem.*, **11** (1905), 404.

(2) A. Fischer and R. J. Boddaert, *Z. Elektrochem.*, **10** (1904), 946.

(3) F. F. Exner, *J. Am. Chem. Soc.*, **25** (1903), 899; *Chem. Zentr.*, **74** (1903), (2), 1210.

(4) L. H. Ingham, *J. Am. Chem. Soc.*, **26** (1904), 1270; *Chem. Zentr.*, **75** (1904), (2), 1758.

was comparatively great, (2) the quantity of the sodium acetate was comparatively small, (3) the current density was comparatively small, (4) the temperature of the electrolyte was comparatively high, and (5) the rotation of the anode was comparatively quick. (B) In the cases reverse to the above, zinc tended to deposit in a spongy form giving a positive error.

The author investigated further by adjusting the factors and found out a method for the electrolytic determination of zinc. This method is very convenient and give very accurate results. It is carried out as shown below.

(1) The sample was used in the form of zinc sulphate, 6 g. of crystalline sodium acetate and various amounts of acetic acid being added. Water was added up to 125 c.c., and the solution was electrolyzed. (2) The concentration of the acetic acid was adjusted according to the amount of zinc present: for 0.5 g. of zinc, 0.15-0.21 normal; for 0.3 g., 0.21-0.27 normal; and for 0.1 g., 0.27-0.33 normal. (3) The electrolysis was begun at room temperature. The regulation of the temperature of the electrolyte was unnecessary. (4) The anode was rotated at the rate of 1500-1700 turns per minute. (5) The current density was maintained at 0.5-0.6 amp./dm^2, till the potassium ferrocyanide reagent ceased to give the reaction of zinc—the main electrolysis—and it was then raised to 3-4 amp. and continued for about 10 minutes. (6) The duration of the main electrolysis varied from about 35 minutes to about 80 minutes according to the amounts of zinc: for 0.5 g. zinc, 65-80 min.; for 0.3 g., 50-60 min.; for 0.1 g., 35-40 min.; and for 0.001 g., 0 min. (7) At the end of the electrolysis, the cathode was washed with water without stopping the current and the rotation of the anode, then washed with alcohol, and ether, dried, and weighed. (8) In these experiments, the errors were always within 0.1 mg.

The influences of such substances as sodium sulphate, ammonium sulphate, ammonium acetate, sodium chloride, and sodium nitrate on the zinc deposition was investigated. The presence of sodium sulphate, ammonium sulphate, and ammonium acetate had no significantly harmful influence, when their concentration was lower than 0.15 normal. The nitrate greatly retarded the deposition of zinc and tended to deposit the metal in a spongy form. The effect of the chloride was not nearly so bad as that of the nitrate, and still it was often a cause of negative error.

The author wishes to express his sincere thanks to Prof. Motooki Matsui, under whose guidance and encouragement this work was carried out.

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