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Bruce A. Lamping

Thomas J. O'Keefe

Missouri University of Science and Technology

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Evaluation of Zinc Sulfate Electrolytes by Cyclic Voltammetry and Electron Microscopy

BRUCE A. LAMPING AND THOMAS J. O'KEEFE

A cyclic voltammetric technique has been developed for approximating the quantities of active chemical species present in zinc sulfate electrolytes. The experimental apparatus consisted of a Pyrex "H" cell, an aluminum cathode encased in a Teflon holder, a carbon anode and a mercurous sulfate reference electrode. Voltammograms were obtained using industrial, purified neutral leach solution (Cominco Ltd., Trail, BC) acidified to give a final concentration of 0.77 M Zn^{++} and 1 M H_2SO_4 . The polarization curves were then evaluated and used as reference standards to compare with results obtained when various organic and inorganic additions were made. The deposit morphologies obtained for short-time cathodic cycles were also studied with the aid of a Scanning Electron Microscope. Changes in concentrations of glue in the 5 to 10 ppm range and of antimony in the 5 to 10 ppb range were detected using the techniques described.

THE extraction of zinc from ore by electrowinning is a complex technical operation, but it has been used successfully for decades as one of the primary means of producing this metal. However, there have always been a number of basic problems associated with electrolytic zinc which have made the process difficult to control. Also, over the years the art has often proven to be as important as the science, with extraordinary levels of effort required by operating personnel to maintain an acceptable degree of efficiency.

One of the reasons for this stems from the fact that zinc is electrochemically very active. This makes zinc ion reduction from aqueous solution more involved than for metals whose decomposition or equilibrium potentials are more noble than those of zinc. It has been well documented¹⁻⁵ that the presence of numerous trace impurities, such as Ni, Co, Ge, Sb, Cu, *etc.*, can be very detrimental to the overall current efficiency for zinc deposition. The precise causes or mechanisms associated with this phenomenon are not known in all instances, but they most probably involve a lowering of the hydrogen overvoltage. This causes an excessive amount of hydrogen reduction at the cathode with subsequent gas evolution. The levels of impurities which affect the process or produce this undesirable result will vary with conditions, but concentrations as low as parts per billion (ppb) for some impurities are sometimes sufficient. Various types of chemical interactions in solution and synergistic effects may also occur, which complicate the situation even more. Thus it is usually quite difficult to characterize properly a zinc electrolyte. The conventional chemical analysis techniques presently used are very helpful in many respects, but do not provide data on the electrochemical activity of the various components in solution. Furthermore, in many instances it is the active concentration of the impurity, nor merely the physical amount, which is of greater importance.

A second major area of concern is control of the growth and electrocrystallization processes of the

cathode deposit. If this is not properly maintained and rough or irregular surfaces are obtained, then lowered current efficiencies and difficulties with physical handling can result. This problem is not unique to zinc winning, however, as similar situations are encountered with many other plating processes. One common practice to assist in minimizing dendrite formation is to make additions of about 10 to 40 ppm of organic reagents, such as glue or gum arabic, to the electrolyte.

However, at present, there are no satisfactory methods for checking the concentration of the organic reagent in the zinc cell acid. Only the physical rate of addition or weight of glue put into the cell is known. Thus, direct observation of cathode growth is about the only available means of evaluating the condition of the electrolyte. This causes a considerable time lag before corrective action can be taken. It is also possible for rather extreme variations in the electrochemical behavior of the electrolyte to occur in a relatively short time, with few if any clues as to the cause or remedy. Also, interactions between the organic and certain other inorganic species in solution can occur,⁶ adding still another dimension to the control problem.

Some work has been performed on the analytical detection of impurities in zinc electrolytes^{7,8} using current-potential relationships, but these have not gained wide acceptance. This technique was also used for analyzing impurity concentrations in manganese sulfate electrolytes.⁹ Although substantial research has been conducted on the processes involved in metal deposition in the presence of organic colloids and other chemical reagents,^{10,11} little practical use seems to have been made of the results. There has also been considerable research on the mechanisms of metal deposition at solid electrodes using both single and cyclic voltammetry techniques.¹²⁻¹⁴ Even though such studies appear to be of potential value, there have been few examples where the data or techniques have been applied to the actual practice of metal electrowinning.

Therefore, having some means of determining the electrolyzability or true active chemical nature of a solution would offer some obvious advantages. In this paper a method is described for revealing and evaluat-

BRUCE A. LAMPING is Metallurgist, Homer Research Laboratory, Bethlehem Steel Company, Bethlehem, PA. THOMAS J. O'KEEFE is Professor of Metallurgical Engineering and Senior Investigator (Materials), GCMR, University of Missouri-Rolla, Rolla, MO 65401.

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ing the electrochemical effects of glue and antimony additions to a zinc electrolyte by a combination of cyclic voltammetry and Scanning Electron Microscope (SEM) techniques. The results indicate that this method might also be useful when additives other than glue and antimony are used, thus offering an analytical procedure not presently available for estimating electrolyte behavior.

EXPERIMENTAL PROCEDURE

The cyclic voltammetry experiments were conducted in a Pyrex "H" cell employing a carbon rod counter electrode and a one molar mercurous sulfate reference electrode with an emf of 0.64 V *vs* SHE. The working electrode was made from a 1.22 cm diam rod of aluminum pressed into a Teflon holder. The aluminum rod analyzed 99.99 + pct Al, 0.022 pct Si, 0.003 pct Fe, and 0.003 pct Cu. The area of the aluminum cathode face was 1.18 cm². Before each cycle the aluminum cathode was prepared by polishing with 600 grit Carbitmet paper. The polished surface was then cleaned with an acetone-soaked tissue and finally rinsed with distilled water.

The electrolyte was prepared by taking 327 ml of neutral (pH 5) commercially purified zinc sulfate provided by Cominco Ltd., 55 ml of concentrated sulfuric acid and 618 ml of distilled water. The zinc sulfate electrolyte contained 149 g/l Zn, 1.7 g/l Mn, and the following in mg/l: Cd 0.1, Pb 0.2, Co 0.1, Ge 0.01, Fe 1.5, Ni 0.05, and Cl 97. This gave a solution consisting of 0.77 M Zn and 1 M H₂SO₄. A total of 300 ml of electrolyte and a temperature of 20°C were used for each test. When studying the effects of antimony and glue, these additions were first mixed with the electrolyte in a beaker and then introduced into the "H" cell. Additive stock solutions of 1 g/l were made by dissolving particles of animal glue and potassium antimony tartrate. This minimized any possible concentration gradients which may have resulted if the impurities were pipetted directly into the "H" cell. The aluminum cathode was immersed in the electrolyte for 30 min before the cycle was begun, and prepurified nitrogen was bubbled continuously into both compartments of the "H" cell during the entire experiments. A schematic diagram of the experimental apparatus is shown in Fig. 1.

A sweep rate of 1 mV/s was used for generating the voltammograms shown in Figs. 2 through 7. Other sweep rates were tried but did not give results as consistent as those when the 1 mV/s rate was used. The cycle was set to begin at -0.46 V *vs* SHE with the upper cathodic limit fixed at a value capable of producing a total current of about 50 ma. At this point the process was reversed and was driven anodically to the original starting potential. A maximum cathodic current of 46 ma was attained for deposits whose morphologies were to be studied and the cycle was stopped prematurely when the current decreased to 35 ma on the reverse sweep. At this point the electrode was immediately removed from the cell and washed with distilled water. This procedure was initiated to assure that the deposit morphologies were being compared on an equivalent basis.

RESULTS

A cyclic voltammogram, typical of those obtained for the acidified zinc sulfate solutions investigated, is shown in Fig. 2. Point A is the starting potential and B is termed the decomposition potential for this work. The potential for maximum cathodic current is C which also represents the point at which the sweep direction is reversed. From C the applied voltage proceeds in an anodic direction to D which is the cross-over potential and the point of zero net current flow. The final point, E, represents the potential of maximum anodic current. Thus the curve segment ABC is the cathodic current-cathodic sweep portion while CD is the cathodic current-anodic sweep part of the voltammogram and DEA is the anodic current-anodic sweep portion. The cross-over point seemed to remain fairly constant for most of the runs on the base solutions (0.77 M Zn²⁺, 1 M H₂SO₄). Notable changes (greater than 10 mV) occurred only with large variations in zinc or acid concentration.

Glue Additions

A voltammogram of the type obtained when a 40 ppm glue addition is made to the cell is shown in Fig. 3. In general, the curves for solutions containing glue show increased polarization and higher values of decomposition potential, the degree of which is proportional to the concentration of glue added. Readily detectable changes in overpotential are produced for variations in glue concentration of 5 to 10 ppm.

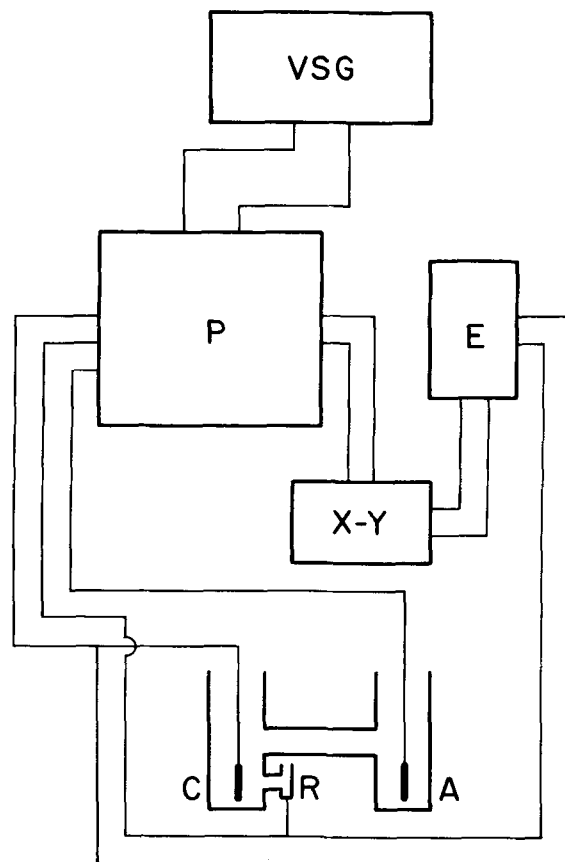


Fig. 1—Schematic for apparatus set-up. VSG = voltage scan generator; P = potentiostat; E = electrometer; X-Y = X-Y recorder; C = cathode; R = reference electrode (mercurous sulfate); A = carbon anode.

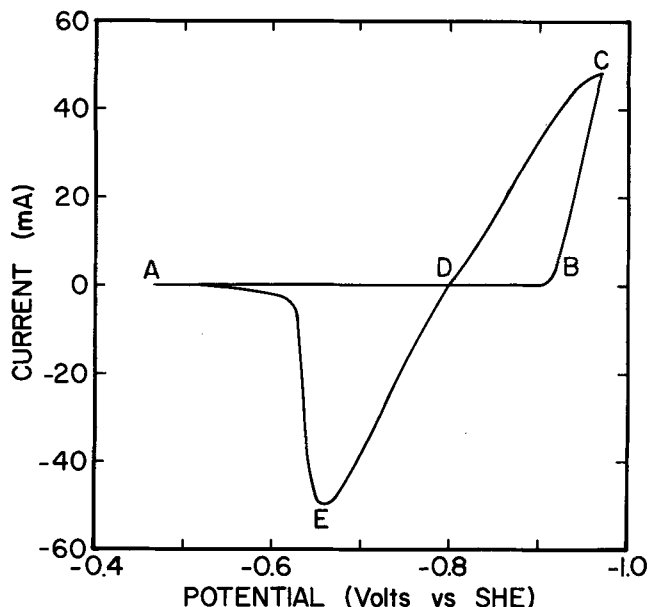


Fig. 2—Cyclic voltammogram for acidified zinc sulfate electrolyte (0.77 M Zn^{++} , 1 M H_2SO_4). A, starting potential; B, decomposition potential; C, reversing potential; D, crossover; E, potential of maximum anodic current. Area of aluminum cathode = 1.18 cm^2 .

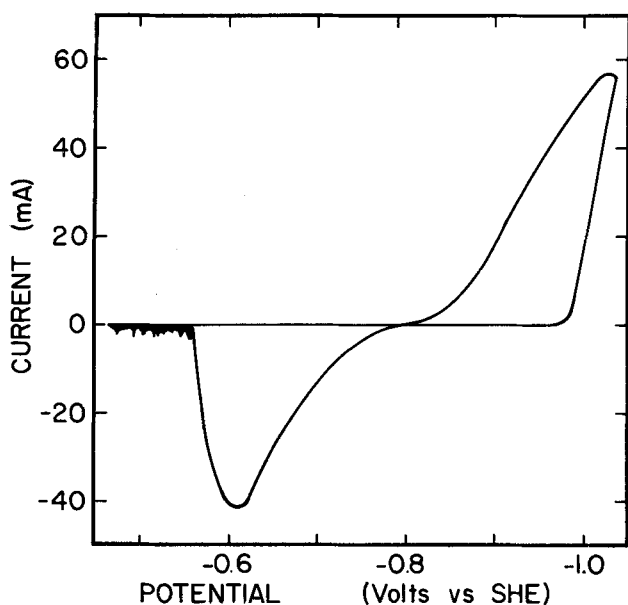


Fig. 3—Cyclic voltammogram for acidified zinc sulfate electrolyte (0.77 M Zn^{++} , 1 M H_2SO_4) containing 40 ppm glue. Area of aluminum cathode = 1.18 cm^2 .

Another distinct characteristic of glue type curves is the decrease in slope as crossover (portion C to D) is approached. As the glue content of the solution increased, the angle of approach to the crossover potential decreased. The relative shape of the anodic current portion of the voltammogram also appeared skewed for glue additions as compared to the fairly uniform or symmetrical shape obtained from pure solutions. It was observed that upon completion of the cycle, zinc flakes floated off the aluminum cathode, indicating incomplete anodic stripping. This accounts for the erratic current fluctuations indicated by the black area on the curve.

Antimony Additions

When antimony is added to the acidified zinc sulfate electrolyte, a voltammogram typical to that in Fig. 4 is obtained. The concentration of Sb for the voltammogram shown is 40 ppb. Antimony additions produce an effect opposite to that resulting from glue additions, in that a marked depolarization occurs. Changes in concentration as low as 5 to 10 ppb Sb can be detected by measuring the change in the deposition potential. This decrease is directly proportional to the concentration of antimony, and was 43 mv lower for a solution containing 10 ppb Sb than for the pure solution. No significant characteristic behavior resulted as crossover was approached (portion CD) and the slope appeared to vary only when large differences between maximum cathodic currents had been attained. It is possible that changes could be found in this vicinity, but they would most likely occur at lower currents, possibly in the microamp range.

Glue and Antimony Additions

Since antimony and glue additions produced opposite effects on polarization curves, studies were also made of solutions containing various ratios of the two. These two reagents are also used in industrial practice to counteract each other. Electrolytes with combinations of 40 ppb Sb with 10, 20, 40 and 80 ppm glue and 20 ppb Sb with 10 ppm glue were examined, with a representative voltammogram shown in Fig. 5. The curve is very similar to that of a pure solution, indicating that the polarization effects caused by these additions when added singly are eliminated when both are present. Solutions with 40 ppb Sb and 40 and 80 ppm glue showed excess glue characteristics (increased polarization for the ABC portion and asymptotic approach to the crossover potential). For 20 ppb Sb with 10 ppm glue and 40 ppb Sb with 20 ppm glue, only a slight glue excess was indicated, but the combination of 40 ppb Sb with 10 ppm glue gave about the same

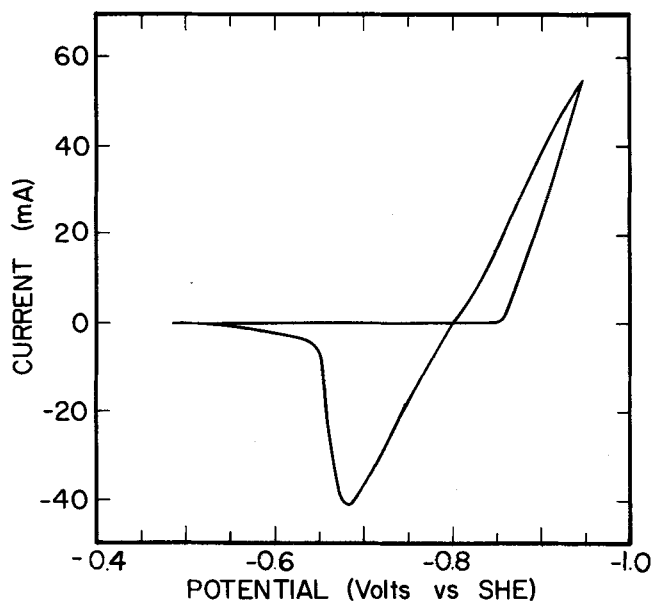


Fig. 4—Cyclic voltammogram for acidified zinc sulfate electrolyte (0.77 M Zn^{++} , 1 M H_2SO_4) containing 40 ppb Sb. Area of aluminum cathode = 1.18 cm^2 .

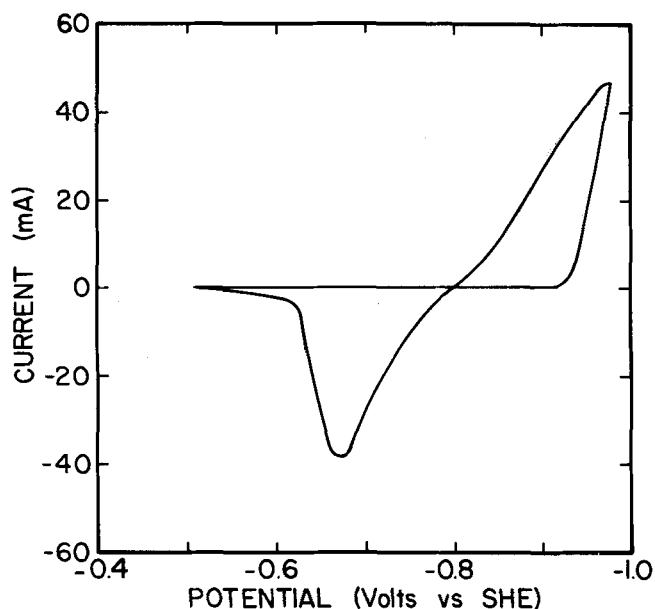


Fig. 5—Cyclic voltammogram for acidified zinc sulfate electrolyte (0.77 M Zn^{++} , 1 M H_2SO_4) containing 40 ppb Sb-20 ppm glue. Area of aluminum cathode = 1.18 cm^2 .

characteristics as the pure electrolyte. Similar ratios, 40 to 80 ppb Sb to 15 to 30 ppm glue, were obtained in another study⁶ in which cathodic current efficiencies were obtained when various glue and antimony additions were made to zinc electrolyte. It was noted for mixed additions, that even with the proper ratio of glue to antimony to produce a cathodic polarization curve resembling that of the pure electrolyte, the slope of the voltammogram is lower as it proceeds through crossover (portion CD). The anodic current portion is skewed, a characteristic of solutions containing glue.

A listing of the cathodic current-potential relationships from voltammograms for various test solutions is given in Table I. Also, the ratio of the area under the anodic curve (ADE) to that under the cathodic curve (ABC + CD) was determined. This a/c ratio gives a rough approximation of zinc deposition efficiency, if it is assumed that both zinc and hydrogen are plated cathodically first and then only zinc is dissolved anodically. Some of the ratios obtained are given in Table II. Although certain trends are indicated, the results obtained seemed less reliable and directly applicable than that derived from the other aspects of procedure described previously. In Figs. 6 and 7 a summary of typical examples of the types of polarization behavior for various test electrolytes is given.

Deposit Morphologies

The various deposit morphologies obtained from electrolyzing both pure zinc solutions and solutions containing antimony or glue were studied using the scanning electron microscope. The coverage was evenly distributed for pure zinc deposits with the average particle size being $5 \mu\text{m}$ as shown in Fig. 8. Each crystal appeared to be growing independently of its neighbors with no tendency for the particles to join together. It is also evident that there is a substantial

Table I. Current (mA) Produced at Specific Potential Intervals Past Crossover for 0.77 M Zn^{++} , 1 M H_2SO_4 Solutions

Concentration	mV Past Crossover (ABC Portion of Curve)						
	50	75	100	125	150	175	200
No additions	0	0	0.25	8.0	28.0	50.0	—
10 ppm glue	0	0	0	0	0.5	9.0	33.0
20 ppm glue	0	0	0	0	0.25	2.5	21.0
40 ppm glue	0	0	0	0	0	0.75	15.0
10 ppb Sb	0	3.0	12.5	26.0	42.0	—	—
20 ppb Sb	0	5.5	16.0	27.0	42.0	—	—
40 ppb Sb	0.5	12.0	25.0	41.0	58.0	—	—
20 ppb Sb-10 ppm glue	0	0	0	3.0	20.0	43.0	64.0
40 ppb Sb-10 ppm glue	0	0	0	5.0	22.0	47.0	68.0
40 ppb Sb-20 ppm glue	0	0	0	2.0	20.0	46.0	66.0
40 ppb Sb-40 ppm glue	0	0	0	0	1.0	19.0	46.0
40 ppb Sb-80 ppm glue	0	0	0	0	0	2.0	18.0

Table II. Relative Zinc Deposition Efficiencies for 0.77 M Zn^{++} , 1 M H_2SO_4 Solutions

Concentration	a/c Ratio
No addition	0.83
10 ppm glue	0.62
20 ppm glue	0.58
40 ppm glue	0.58
10 ppb Sb	0.73
20 ppb Sb	0.57
40 ppb Sb	0.61
20 ppb Sb-10 ppm glue	0.75
40 ppb Sb-10 ppm glue	0.78
40 ppb Sb-20 ppm glue	0.76
40 ppb Sb-40 ppm glue	0.72
40 ppb Sb-80 ppm glue	0.52

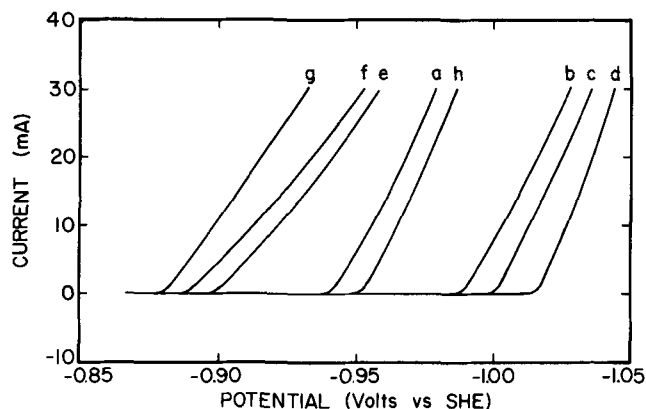


Fig. 6—Polarization curves for ABC portion of voltammogram for acidified zinc sulfate electrolyte (0.77 M Zn^{++} , 1 M H_2SO_4); (a) no additions, (b) 10 ppm glue, (c) 20 ppm glue, (d) 40 ppm glue, (e) 10 ppb Sb, (f) 20 ppb Sb, (g) 40 ppb Sb, (h) 40 ppb Sb-20 ppm glue. Area of Al cathode = 1.18 cm^2 .

portion of the aluminum substrate which remains clear of any zinc, indicating a limited amount of initial nucleation. Deposits from Sb containing solutions showed a marked increase in facet size ($10 \mu\text{m}$ for 40 ppb Sb) and it is surmised that they may have a slight (0002) preferred orientation, however, more investigations would have to be performed to substantiate this. The facet and crystallite size were directly related to Sb concentration as shown in Figs. 9 and 10. There is also no indication that corrosion is oc-

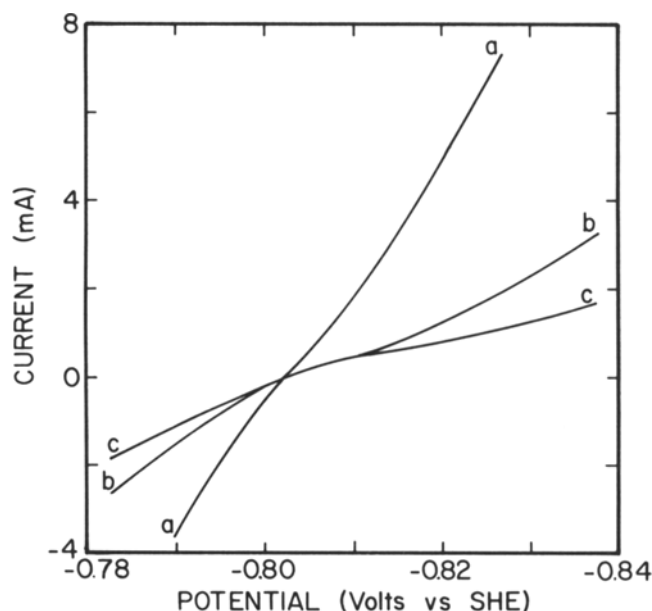


Fig. 7—Polarization curves for expanded CD portion of voltammogram pure acidified zinc sulfate electrolyte (0.77 M Zn^{++} , 1 M H_2SO_4); (a) no additions and 10 ppb Sb, (b) 10 ppm glue, (c) 40 ppm glue. Area of aluminum cathode = 1.18 cm^2 .

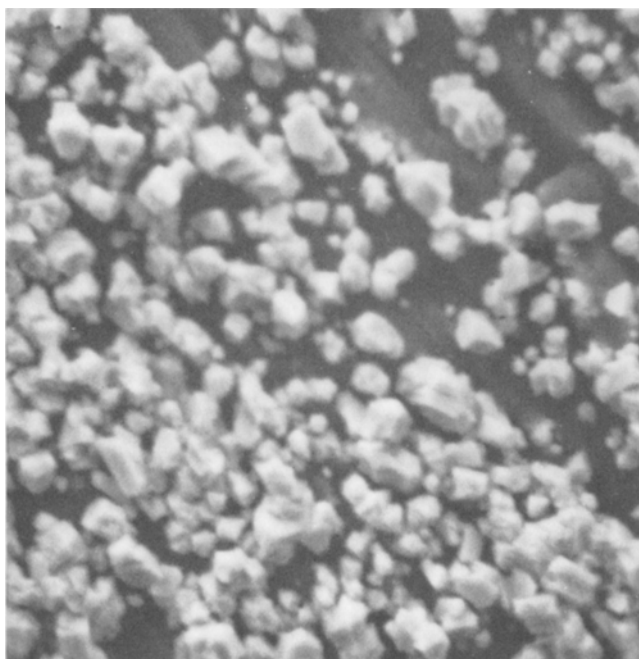


Fig. 8—Scanning-electron micrograph for the deposit obtained from acidified zinc sulfate electrolyte (0.77 M Zn^{++} , 1 M H_2SO_4), magnification 1100 times.

curing, which is usually characterized by pits and irregularities in the facet edges. Glue addition deposits show an average facet size of 1 μm , with distinct preferred orientation characteristics, probably (11 $\bar{2}$ 0).⁶ Zinc deposits produced with glue in solution, or at high overpotentials, also exhibit a characteristic morphology. The dominant feature is the appearance of edges of zinc platelets, with the basal planes lying perpendicular to the electrode. The degree of the edge

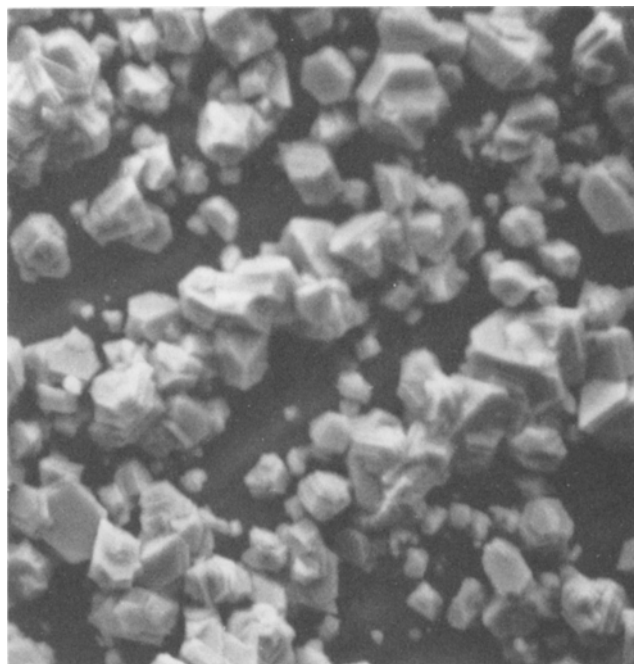


Fig. 9—Scanning-electron micrograph for the deposit obtained from acidified zinc sulfate electrolyte (0.77 M Zn^{++} , 1 M H_2SO_4) containing 10 ppm Sb, magnification 1150 times.

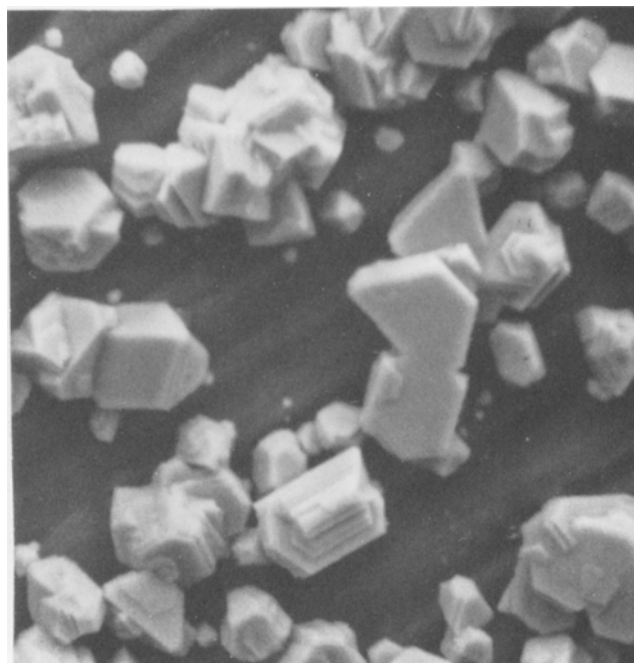


Fig. 10—Scanning-electron micrograph for the deposit obtained from acidified zinc sulfate electrolyte (0.77 M Zn^{++} , 1 M H_2SO_4) containing 40 ppm Sb, magnification 1150 times.

type growth becomes greater as the amount of glue increases. This is illustrated in Figs. 11, 12 and 13, which are representative of structures made with 10, 40 and 80 ppm glue, respectively, in solution. The individual crystals (about 8 μ) also tend to agglomerate more than those for pure zinc or Sb addition deposits. Each agglomerated "island" appears to run parallel to the striations on the aluminum surface.

The structure obtained when 40 ppb Sb and 20 ppm

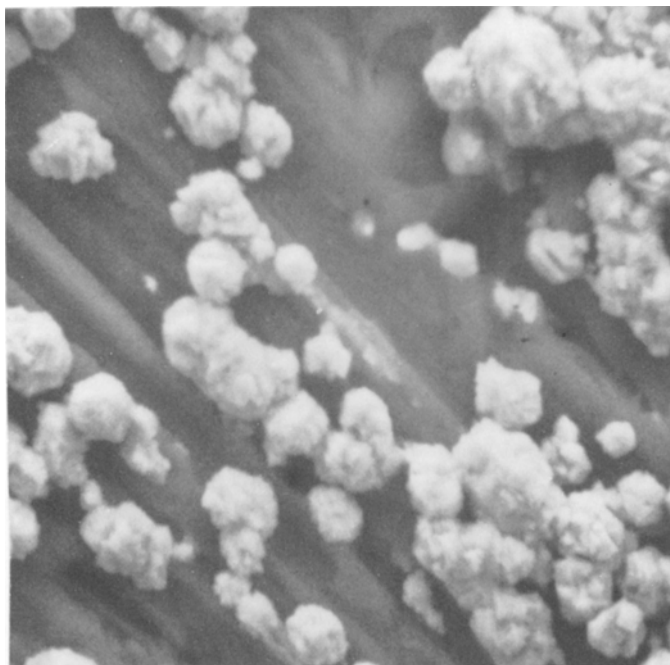


Fig. 11—Scanning-electron micrograph for the deposit obtained from acidified zinc sulfate electrolyte (0.77 M Zn^{++} , $1 \text{ M H}_2\text{SO}_4$) containing 10 ppm glue, magnification 1100 times.

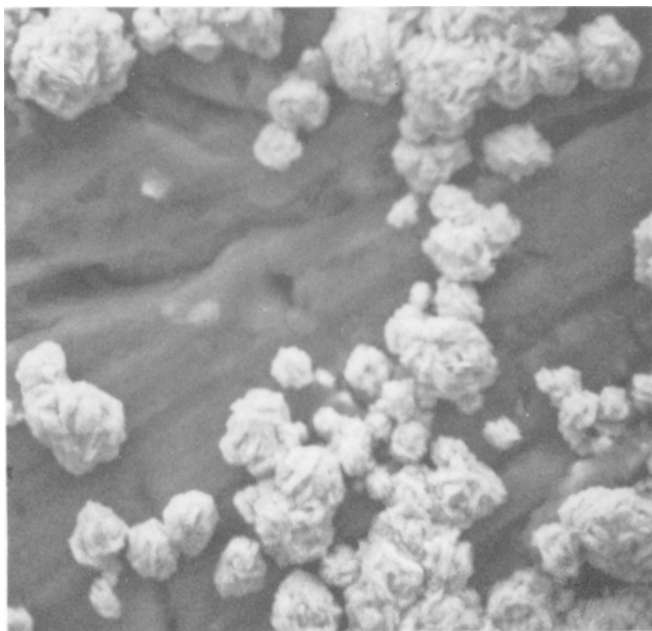


Fig. 12—Scanning-electron micrograph for the deposit obtained from acidified zinc sulfate electrolyte (0.77 M Zn^{++} , $1 \text{ M H}_2\text{SO}_4$) containing 40 ppm glue, magnification 1040 times.

glue were both added to the zinc electrolyte is shown in Fig. 14. The morphology doesn't show the distinct characteristics of either the Sb or glue, but approaches that for the unaltered solution. There might be an appearance of a slight excess glue type structure, but in general, it seems that the two additives counteract each other. Again, as with the polarization data, there are strong indications that the individual effects of glue or antimony on the process are eliminated if

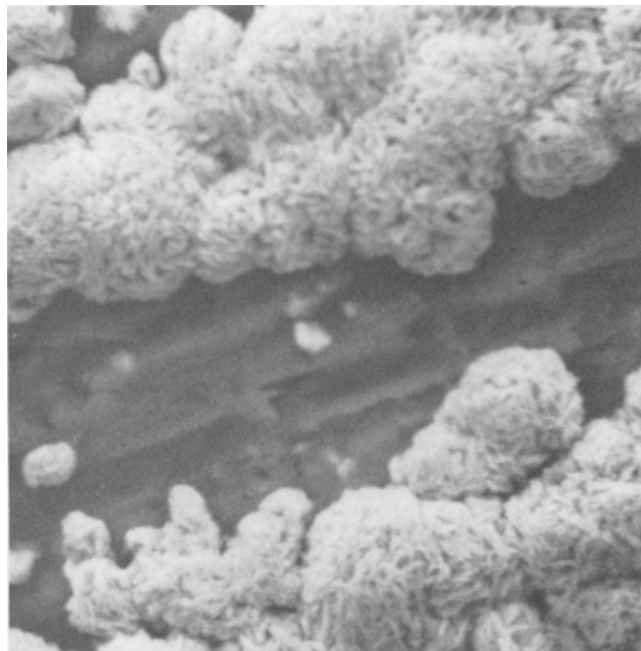


Fig. 13—Scanning-electron micrograph for the deposit obtained from acidified zinc sulfate electrolyte (0.77 M Zn^{++} , $1 \text{ M H}_2\text{SO}_4$) containing 80 ppm glue, magnification 1100 times.

both reagents are present in the proper ratio. The mechanism or cause for the decreased electrochemical activity is not known, but could result from a chemical interaction between the two in bulk solution or possibly some more complex phenomena occurring in the double layer vicinity.

DISCUSSION OF RESULTS

The data given previously show conclusively that the results of cyclic voltammetry tests are quite sensitive to the presence of two types of impurities or additives in zinc sulfate electrolyte. In particular, this method should permit determination of the amount of electrochemically active organic reagent in the solution. However, it might be necessary to run a series of calibration tests using the specific organic additive and electrolyte. It also appears that testing of this type should allow not only an evaluation of the quality of the electrolyte but should also provide some insight into the specific type of impurity present.

Although only glue and antimony were studied extensively, preliminary tests showed that other impurities and additives might also be characterized by this method. Aside from the valuable practical information generated, this method should lead to a better understanding of the more basic aspects of the behavior of additives and impurities in zinc electrolysis.

When an addition is made to a pure zinc solution, it might be expected to affect the deposition mechanism in two major ways. It may either change the overpotential for zinc deposition or for hydrogen evolution, or possibly both. In the case of glue additions, both the zinc deposition and hydrogen overvoltages on aluminum seem to increase. This would account for the increased decomposition potential (portion ABC of the voltammetric curve) when glue is present. It

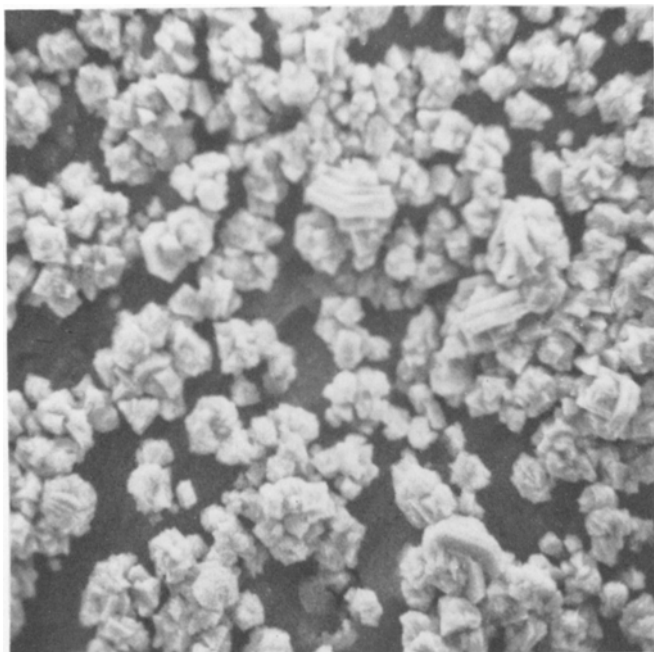


Fig. 14—Scanning-electron micrograph for the deposit obtained from acidified zinc sulfate electrolyte (0.77 M Zn^{++} , $1 \text{ M H}_2\text{SO}_4$) containing 40 ppb Sb-20 ppm glue, magnification 1080 times.

appears that glue also increases the zinc deposition potential on previously deposited zinc as shown by the decreased slope of the polarization curve near crossover. This substantial deposition overpotential is probably due to the overvoltage required for the zinc to deposit through the glue adsorption layer¹⁰ which affects the charge transfer rate. Glue also must increase the hydrogen overpotential, but to a lesser degree than it changes the zinc overpotential because of the smaller ratio of anodic to cathodic curve areas. Antimony, on the other hand, decreases the overpotential for both zinc deposition and hydrogen evolution on aluminum as shown by the decreased cathodic decomposition potential and the decreased ratio of anodic to cathodic curve areas. It does not, however, appear to affect the deposition overpotential onto previously deposited zinc, at least for the short deposition times used in these experiments. This is surmised from noting that the approach to crossover is very similar to that for pure zinc solutions. A few preliminary curves in which the cathodic range was decreased were made on a pure solution and on one containing approximately 100 ppb Sb. Even though the extent of the work was insufficient to allow any definite conclusions, a noticeable trend did occur. The total cathodic current for the pure solution was less than that for the antimony solution. The amount of zinc deposited, as evidenced by the anodic to cathodic area test, was small for the pure solution but there was absolutely no indication of any zinc deposition with the antimony solution. Thus, it might be inferred that at lower current densities, the antimony either enhances the hydrogen reduction reaction or causes any zinc that is deposited to redissolve or possibly both. It was shown that antimony had the tendency to give a low relative zinc plating efficiency, but it also seems that it has a greater influence on the hydrogen to zinc

ratio at lower current density than at higher values when an aluminum cathode is used.

The morphologies obtained when glue was added were different from those obtained with pure zinc electrolyte. One of the most noticeable effects was the apparent preferred orientation. It is known¹¹ that certain facets and orientations were obtained under various process conditions and that the electrocrystallization is most influenced by current density and overpotential. When the Bravais law of crystal growth is obeyed, the most densely packed planes should have the slowest rate of growth. Also those facets which have the greatest metallic overpotential are the slowest growing ones. For the deposition of zinc this is the (0002) plane. By simple geometric arguments, it can be shown that the fastest growing facets will grow out of existence and the slower growing ones will survive. For free and lateral growth conditions, these (0002) facets will grow parallel to the substrate and survive, while the fast growing (10·1), (10·2) and (10·3) planes grow into one another and are eliminated. Zinc has a rather low metallic overpotential and therefore a lateral growth mode would be favored. An outward growth mode would be more typical for growth at higher overpotentials. The presence of glue causes an inclination of the basal planes, in that growth tends to become more outward than lateral. The glue is therefore increasing the overvoltage on preferentially selected planes and thus impeding the free growth of zinc. The glue also seems to cause increased nucleation, giving a substantial decrease in facet size. The agglomeration of the crystals obtained with high glue concentrations is probably due to a large number of microscopic "bridges" passing through pores in the glue adsorption layer and setting up nucleation sites for further deposition.

The morphology obtained with antimony additions is most marked by the large crystal facets which appear to have a slight preferred orientation with the (1120) planes parallel to the aluminum substrate as compared to those for pure zinc solutions. The role of antimony as a catalyst in the evolution of hydrogen may cause the hydrogen to absorb on preferentially selected planes and inhibit zinc nucleation. The slower the nucleation rate, the greater the crystal girth which explains the increased facet size for anti-mony addition deposits.

For simultaneous additions of glue and antimony the morphology took on the characteristics of both. The facets appear to be oriented in a mode similar to those for glue-like deposits (*i.e.*, outward growth, small facet size). However nucleation appeared to be more uniform over the entire aluminum surface.

CONCLUSIONS

It has been shown that cyclic voltammetry techniques may be used to characterize certain zinc electroplating solutions. The method developed was particularly sensitive to the effects of antimony, glue or combinations of the two. Changes in concentration of about 10 ppb of antimony and 10 ppm glue were readily detectable by comparing polarization behavior for these solutions with those for pure, unaltered electrolyte. The features of the polarization curves

which seemed most susceptible to change were the decomposition potential, angle of approach to equilibrium potential during an anodic sweep, and shape of the anodic current portion of the curve. Morphologies of short-time deposits were also examined and good correlations between structure and active additives in solution were obtained. Thus it appears that a combination of cyclic voltammetry and scanning microscopy, or possibly either individually, may be used to gain valuable information about zinc sulfate electrolytes for possible applications to industrial plant practice and control, or in research as well.¹⁵

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