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Detection of impurities in zinc sulfate electrolytes by cyclic voltammetry techniques.

Bruce Alan Lamping

DETECTION OF IMPURITIES IN ZINC SULFATE ELECTROLYTES

BY CYCLIC VOLTAMMETRY TECHNIQUES

BY

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T. J. O'Keefe (Advisor)   _W. J. James_

David Wolf

ABSTRACT

A cyclic voltammetric technique has been developed for quantitatively detecting the presence of active chemical species present in zinc sulfate electrolytes. The experimental apparatus consisted of a pyrex "H" cell, an Al cathode encased in a Teflon holder, a carbon anode and a mercurous sulfate reference electrode. Voltammograms were obtained from industrial, purified neutral leach solution (Cominco Ltd., Trail, B.C.) acidified to give a final concentration of 0.77 M Zn^{++}, 1 M H_2SO_4. The polarization curves were then evaluated and used as a reference standard to compare with results obtained when various organic and inorganic additions were made. The principal single additions made were glue, Sb, Cu, Ag, and Ni, while mixtures of glue and Sb were also tried. The method was capable of detecting the presence of Sb in the concentration range of 5-10 ppb; Cu, Ag, and Ni in the 1-5 ppm range; and glue in the 5-10 ppm range.

Investigations on the deposit morphologies as affected by additions were made with the aid of a scanning electron microscope (SEM) and a non-dispersive X-ray spectrometer was used to locate impurities on the Al electrode surface. It was also possible to estimate the nature and concentration of the additives by the morphology changes which resulted.

ACKNOWLEDGEMENTS

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INTRODUCTION

The extraction of zinc by electrowinning is a complex process with many factors involved in its technical and economic success.

It is known that certain trace impurities in a zinc electrolyte can be very detrimental to the efficiency of the process. Many times, regardless of the degree of care and control, the possibility still exists that impurities remain in the final solution.

In most instances, impurity concentration levels in the parts per million (ppm) or even parts per billion (ppb) range are sufficient to reduce current efficiencies. Since the harmful impurity levels allowable are so low and because synergistic effects quite often occur, it is difficult to evaluate the electrolyzability of a zinc solution. Because of this, the deleterious effects of the impurities do not become evident until the actual electrolysis takes place, which makes corrective action very difficult. It would be extremely beneficial if a rapid and accurate method could be perfected to allow some predictions to be made as to the quality of the electrolyte prior to introducing it into the electrolytic cells. It would also be desirable if a method could be perfected to examine the nature of the

process from a mechanistic standpoint rather than the more qualitative rapid test techniques which only consider short time deposition efficiencies.

In this work cyclic voltammetry techniques have been used to attempt to characterize zinc sulfate electrolytes by obtaining a correlation between the type and concentration of various additives and their respective polarization curves. The data were also evaluated from the standpoint of gaining additional insight into the more fundamental aspects of the behavior of these additions.

The bulk of the experimental work was performed on solutions containing additives such as glue, antimony, silver, copper, and nickel. Scanning electron microscopy (SEM) of various short time deposits was also completed on a number of the samples to determine any morphological changes.

LITERATURE REVIEW

Numerous studies have been conducted on the effects of trace impurities in zinc electrolytes. Mantell (1) has compiled a list of the maximum impurity levels which can be tolerated in the zinc electrolyte while high efficiencies are still maintained during electrolysis. Antimony, germanium, cobalt, copper, and nickel, to name a few, were found to be detrimental in the ranges of 0.5, 0.001, 1, 10, and 0.01 ppm respectively. Mathewson (2) has also commented on the various concentration levels allowable.

A study on the effect of Co additions to pure zinc sulfate electrolytes by Wark (3) showed that 100 pppm Co caused very poor efficiencies as the temperature was increased from 20 to 50°C or the current density (c.d.) was decreased from 60 to 30 asf. The Co was co-deposited with the zinc and provided a surface for enhanced hydrogen evolution and also set up local cells for zinc dissolution.

Fukubayashi (4) has categorized impurities by the affect they had on current efficiency, morphology, and the apparent mechanism for hydrogen evolution. The results of his work indicated that the structure and morphology of the deposit were important in determining the acceptable concentration of any given impurity.

Investigations pertaining to the influence of combinations of as many as four impurities, present simultaneously in the electrolyte, on the efficiency of zinc deposition were made by Steinveit and Holtan (5). They found that there is no law of additivity for the influence of impurities and therefore the presence of only one of two impurities may not harm the electrolysis at all. However, when certain impurities are present simultaneously, synergistic effects may occur. The combined effect of Sb and Co was considerably more detrimental than the effect of either additive individually. They further found that if a deposit was forme from a pure solution, it was possible to start corrosio: of the deposit by adding the proper combinations of impurities to the solution.

Robinson and O'Keefe (6) determined that a rather wide variation in glue concentration can be tolerated with only a slight penalty in current efficiencies. Excessive glue concentrations, however, caused the zinc deposit to part from the aluminum starting sheets and eventually short across to the anodes. They also investigated glue and antimony additions and found that ratios of 40-80 ppb Sb to 15-30 ppm glue gave optimum efficiency.

A study of the effect of glue additions on the morphology of zinc deposits and the polarization curve for zinc deposition was made by Geilow (7). It was demonstrated that the orientations changed from a more lateral mode of growth to a more outward mode of growth or in other words from a (0002) orientation to a (11$\bar{2}$0) orientation, with higher glue concentration. Glue also acted as a nucleation agent and caused considerable change in grain size and orientation with increased concentrations.

Cole (8) has done studies on the influence of temperature and c.d. on orientation and morphology of zinc deposits. He showed certain correlations between the Bravais law and overpotential in determining which crystallographic facet orientations preferentially formed. A similar study was conducted by Reddy (9) for nickel deposition.

An extensive study of the electrochemistry of metals and adsorption on electrode surfaces has been done by Kabanov (10). The mechanism of metal deposition through organic colloids and hydrogen adsorption layers and their destruction by other additives was investigated. It was found that halide ions were particularly effective in disrupting the adsorption layer of tetrabutyl-ammonia in a cadmium sulfate electrolyte. Other relationships for different metal-electrolyte systems with film disrupting agents were discussed.

It was postulated that, in order for metal to deposit, the metal ions must penetrate to the electrode through the adsorption layer. The overvoltage associated with this step was termed "penetration" overvoltage with its magnitude depending on the nature of the ions and adsorption layer. In thin adsorption layers the metal may be deposited on the adsorption layer because of many microscopic bridges passing through pores in the layer. In these instances the adsorbed species can be incorporated into the deposit.

Some work has also been performed on the analytical detection of impurities in electrolytes. Maja and Spinelli (11) conducted experiments in which zinc was deposited at a constant current on the internal surface of a hollow drilled into an aluminum electrode. Voltage oscillations resulted when hydrogen bubbles formed in the hollow were periodically released. Depending on the type and concentration of impurity, these oscillations occurred with different frequencies. They concluded that hydrogen evolution does not depend on the amount of impurity deposited with the zinc, but on the extension of the surface-contaminated zones of the cathode because hydrogen evolution occurs at those zones with a lower overvoltage. It was observed that zinc dissolution starts in the pores of the deposit and the electrolyte

in the pores was renewed with difficulty, because of evolving hydrogen. Zinc deposition was greatly reduced in this area which allowed the impurities to remain exposed and serve as sites for hydrogen evolution.

Current-potential curves were used by Ferment (12) for analyzing impurity level concentrations in manganese sulfate electrolytes. Certain chemical species gave a correlation between current and concentration of impurity. The current-potential curves showed an initial region where the hydrogen evolution reaction predominated, but as the cathodic potential increased a limiting current was reached. This represented a transition point at which an increased cathodic potential caused the manganese to co-deposit with hydrogen. The transition current was found to shift depending on the impurity level present. It was concluded that the potential shift was indicative that the hydrogen reaction was occurring on deposited manganese as well as on the stainless steel electrode. This point was also thought to represent the stage at which a sufficient quantity of manganese nuclei had formed to allow the electrode to behave as a manganese surface rather than as a stainless steel one. Ferment also concluded that the impurities were electrodeposited and that the amount of impurity which could be tolerated decreased as the plating time increased because the

impurities significantly affect the hydrogen overvoltage. Vennesland, Holtan, and Solhjell (13) conducted polarization experiments similar to those of Ferment using zinc sulfate electrolytes. Transitions were found in these polarization curves as well, but were less definitive than those produced with manganese.

Cyclic voltammetry was first employed by Seveik (14) and since then numerous studies of electrode mechanisms have been made by employing this technique (14, 15, 16, 17, 18, 19). In cyclic voltammetry, the potential was driven at a predetermined rate both cathodically and anodically. The corresponding current was recorded usually either by an X-Y recorder or an oscilloscope. Nicholson and Shain (15) showed that for irreversible systems both the peak potential and the half peak potential were functions of the rate of potential scan but were not for reversible systems. They calculated that the shift in potential was about $30/\alpha n$ millivolts (cathodic for a cathodic scan) for each ten fold increase in the rate of potential scan for a totally irreversible system, where α was the charge transfer coefficient and n was the number of electrons. Adams (14) has also commented on the effect that irreversible systems have on cyclic voltammograms and he states that a higher polarization overpotential results with increasing

sweep rates, causing the voltammograms to appear to be flattened out.

Considerable work has been done with single sweep voltammetry which is distinguishable from cyclic voltammetry on the basis that only the anodic sweep or the cathodic sweep is carried out. Many of the theoretical aspects determined from single sweep voltammetry however, can also be applied to cyclic voltammetry.

The reversible depositon of metals on solid electrodes was studied by Manning and Mamantov (20, 21, 22) using single sweep voltammetry techniques. Ag, Fe and Ni were found to exhibit reversible tendencies as determined from their respective voltammograms. Kabanov (10) on the other hand has shown the deposition of zinc to be a rather irreversible reaction, Will and Knorr (23) have studied the hydrogen ionization reaction by single sweep voltammetry and have shown it to be a relatively reversible one.

Single sweep voltammetry as it relates to the determination and significance of adsorbed intermediates was investigated by Conway, Gileadi, and Angerstein-Kozlowska (24). They concluded that the charge passed in a process in which deposition or ionization of an intermediate is involved, will depend on the potential scan rate.

Voltammetry has proven to be an invaluable asset in characterizing electrochemical reactions as to controlling mechanisms, charge transfer rate, and the possible formation of intermediate species.

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 0.64V vs. S.H.E. The working electrode was made from a 0.61 cm. diameter rod of aluminum pressed into a Teflon holder. The Al rod analyzed 99.99 + % Al, 0.002% Si, 0.003% Fe, and 0.003% Cu. The area of the Al cathode face was 1.18 cm^2. More specifications on the design of the aluminum cathode are given in Appendix 1. Before each cycle the aluminum cathode was prepared by polishing with 600 grit Carbimet paper with the final pass being made on an unused portion of the paper. The polished surface was then cleaned by patting it with an acetone soaked tissue and finally rinsing with distilled water.

The electrolyte was prepared by taking 327 ml of neutral purified zinc sulfate, (pH 5), provided by Cominco Ltd. from their sulfide leach circuit, 55 ml of concentrated sulfuric acid and 618 ml of distilled water to obtain an approximate 1 M H_2SO_4, 0.77 M Zn electrolyte. For each experiment 300 ml of electrolyte was introduced into the "H" cell. When studying the effects of antimony and glue, these additons were first mixed with the electrolyte in a beaker and then introduced into the "H"

cell. This overcame any possible concentration gradients which may have resulted if the impurities were pipetted directly into the "H" cell. The Al cathode was immersed in the electrolyte for 30 minutes before the cycle was begun, and prepurified nitrogen was bubbled continuously into both compartments of the "H" cell during the entire experiment.

A Wenking model VSG72 voltage scan generator was used to drive a Wenking Potentiostat model 70HP10, and the cyclic voltammograms were recorded with a Moseley 135AM X-Y recorder. A schematic of the experimental setup is shown in Figure 1.

Various sweep rates were tried with 1 mV/sec. giving the most consistent results. The cycle was set to begin at -0.46 V vs. S.H.E., with the upper cathodic limit set to 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. For deposits whose morphologies were to be studied, the maximum cathodic current attained was 46 ma, 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 a relatively equal basis.
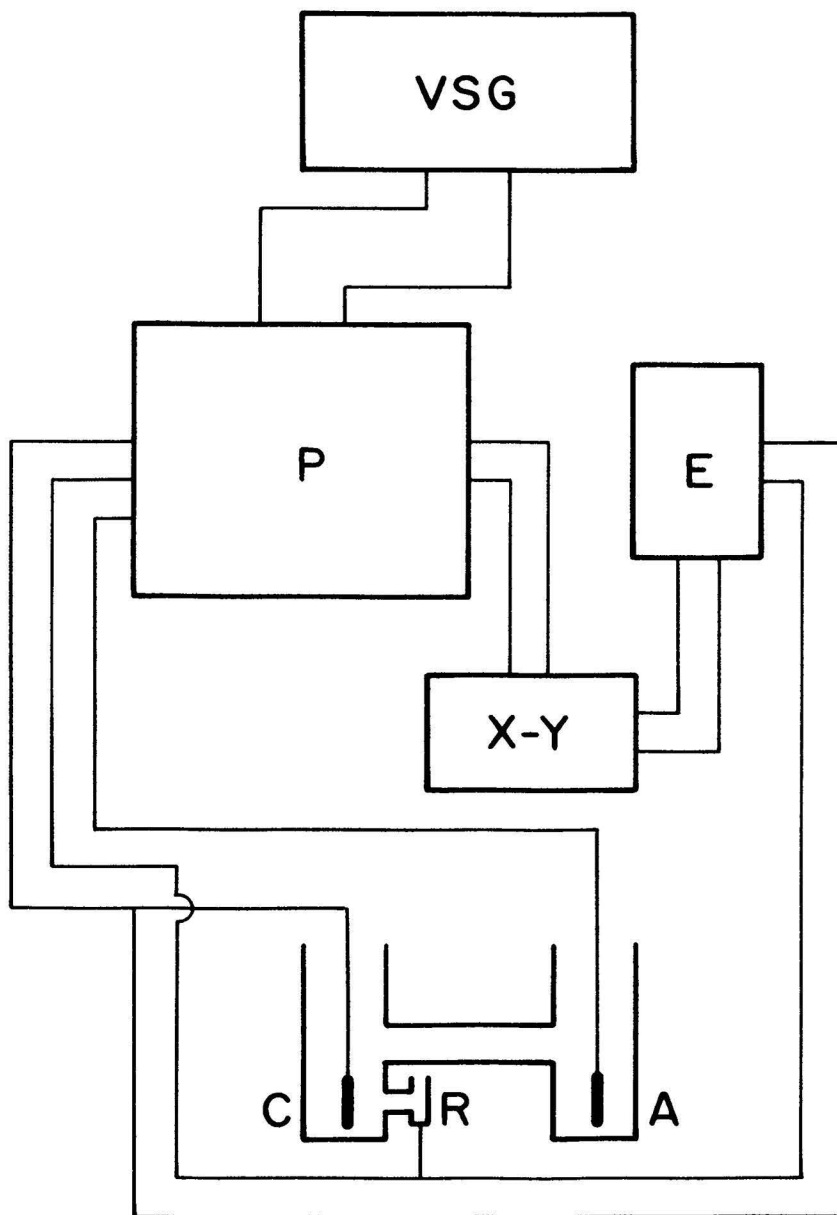
FIGURE 1. SCHEMATIC FOR APPARATUS SET-UP. VSG =
VOLTAGE SCAN GENERATOR; P = POTENTIOSTAT;
E = ELECTROMETER; X-Y = X-Y RECORDER;
C = Al CATHODE; R = REFERENCE ELECTRODE
(MERCUROUS SULFATE); A = CARBON ANODE.

The procedure used for studying the effects of Cu, Ag and Ni was altered from that described previously in that the cathode was held in contact with the electrolyte at open circuit potential for considerably longer periods of time (12 to 48 hours).

RESULTS

A cyclic voltammogram, typical of those obtained for the acidified zinc sulfate solutions investigated, is shown in Figure 2. Point A is the starting potential and point B is termed the decomposition potential for this work. The point of maximum cathodic current is C which also represents the potential at which the sweep direction is reversed. From point C the reaction proceeds in an anodic direction to point D, which is the crossover potential and the point of zero net current flow. The final point, E, represents the potential of maximum anodic current. Thus the curve ABC is the cathodic current-cathodic sweep portion while CD is the cathodic current-anodic sweep part of the voltammogram and curve DEA is the anodic current-anodic sweep portion. The crossover point seemed to remain fairly constant for most of the runs on the base solutions (0.7 M Zn^{++}, 1 M H_2SO_4) even when small quantities of impurities were added. Notable changes (greater than 10 mV) occurred only with large variations in zinc or acid concentration.

The results obtained from voltammograms for the various solutions are compared on the basis of the current level attained at certain potential intervals past crossover which gives a relative measure of the
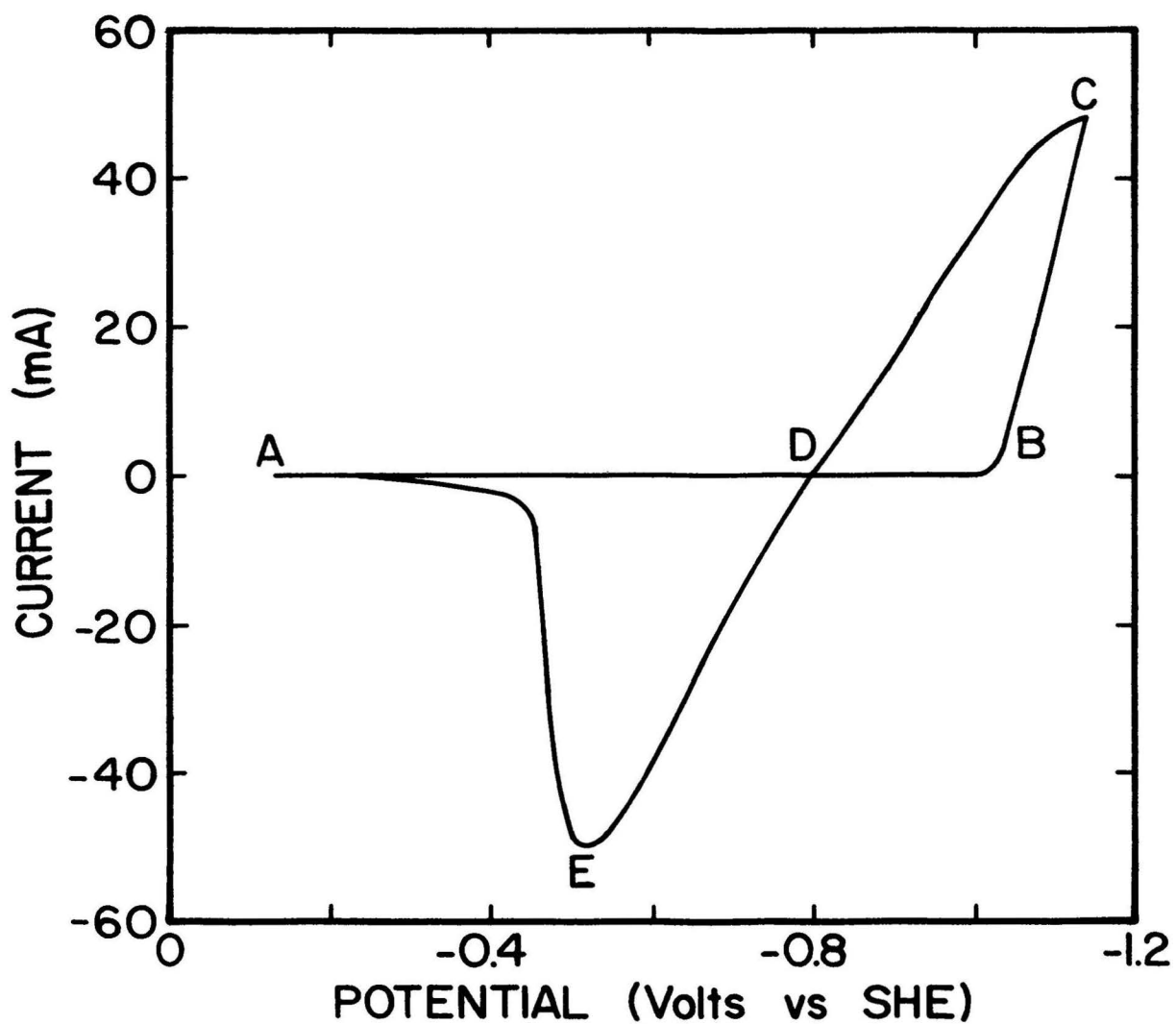
FIGURE 2.   CYCLIC VOLTAMMOGRAM FOR ACIDIFIED ZINC SULFATE
ELECTROLYTE (0.77 M Zn^{++}, 1 M H$_2$SO$_4$).   A,
Starting potential; B, Decomposition potential;
C, Reversing potential; D, Crossover; E,
Potential of maximum anodic current.   Area of
aluminum cathode = 1.18 cm^2.

polarization. These values are given in Table I for the corresponding plots shown in Figures 3-9. It should be noted that the current can be converted to c.d. by dividing by the cathodic area 1.18 cm^2, and that the sweep rate was held constant at 1 mV/sec. The ratio of the area under the anodic curve (ADE) to the area under the cathodic curve (ABC + CD) was determined in order to establish a a relative value for zinc depositon efficiency. These ratios are also given in Table II.

Pure Solutions

The voltammogram obtained for pure 1 M H_2SO_4 solutions is shown in Figure 3. As expected, no anodic current is indicated since the only reaction occurring is the evolution of hydrogen.

Pure neutral zinc sulfate solutions produced voltammograms similar to the one shown in Figure 4. Both the crossover and decompositon potentials are lower than those produced by the acidified zinc electrolyte. The slope is also lower, as can be seen by comparing with Figure 5, which is for a 0.7 M Zn^{++} and 1 M H_2SO_4 solution without any additives.

Glue Additions

A voltammogram of the type obtained when glue additions were made is shown in Figure 6. 40 ppm glue was

TABLE I

CURRENT (MA) PRODUCED AT SPECIFIC POTENTIAL INTERVALS PAST CROSSOVER FOR

0.77 M Zn^{++}, 1 M H_2SO_4 SOLUTIONS

	mV Past Crossover (ABC Portion of Curve)						
CONCENTRATION	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 I (Continued)

mV Past Crossover (CD Portion of Curve)

CONCENTRATION	10	20	30	40	50	60	70
No additions	2.50	5.25	8.00	11.50	15.00	17.00	19.00
10 ppm glue	1.00	2.00	3.50	5.25	7.50	10.00	13.00
20 ppm glue	0.75	1.50	2.50	3.50	6.0	8.50	11.00
40 ppm glue	0.50	1.00	1.50	2.50	3.50	5.00	7.50
10 ppb Sb	2.50	5.50	9.00	13.00	17.50	21.50	25.00
20 ppb Sb	2.00	4.50	7.50	11.00	15.00	19.00	23.00
40 ppb Sb	2.50	5.50	9.00	13.00	17.00	21.00	26.00
20 ppb Sb - 10 ppm glue	1.00	3.00	5.00	8.00	11.00	13.00	15.00
40 ppb Sb - 10 ppm glue	1.00	3.50	6.50	9.50	13.00	18.00	22.00
40 ppb Sb - 20 ppm glue	1.00	2.00	3.00	4.50	7.00	10.00	13.00
40 ppb Sb - 40 ppm glue	0.50	1.25	2.00	3.25	4.50	6.50	9.00
40 ppb Sb - 80 ppm glue	0.50	1.25	1.75	2.25	3.00	4.00	5.00

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

SWEEP RATE	a/c RATIO
1 mV/sec	0.83
5 mV/sec	0.71
10 mV/sec	0.68
50 mV/sec	0.48
100 mV/sec	0.46
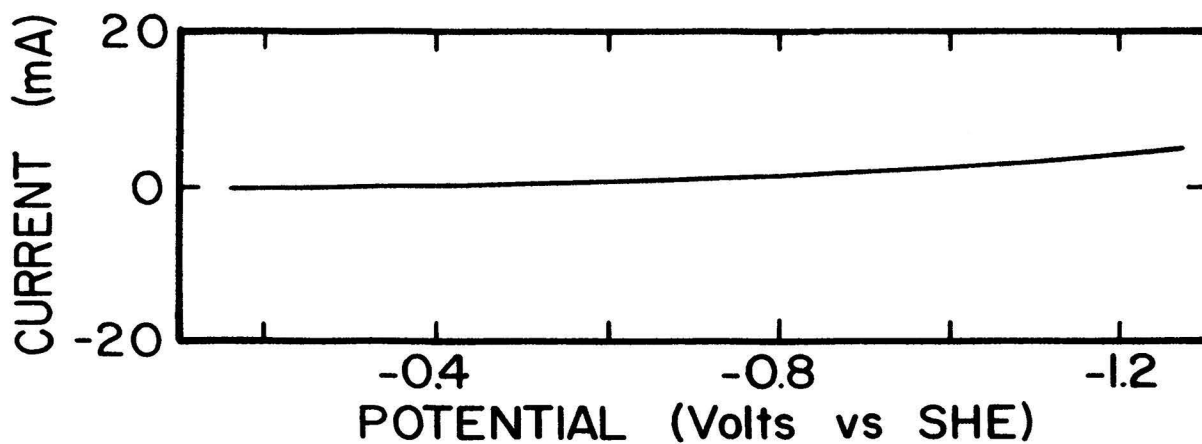
FIGURE 3. CYCLIC VOLTAMMOGRAM FOR 1 M H_2SO_4. Area of aluminum cathode = 1.18 cm^2.

FIGURE 4. CYCLIC VOLTAMMOGRAM FOR NEUTRAL PURIFIED ZINC SULFATE ELECTROLYTE (0.77 M Zn^{++}, pH = 5.0). Area of aluminum cathode = 1.18 cm^2.

FIGURE 5.   CYCLIC VOLTAMMOGRAM FOR ACIDIFIED ZINC SULFATE
ELECTROLYTE (0.77 M Zn^{++}, 1 M H_2SO_4).   Area of
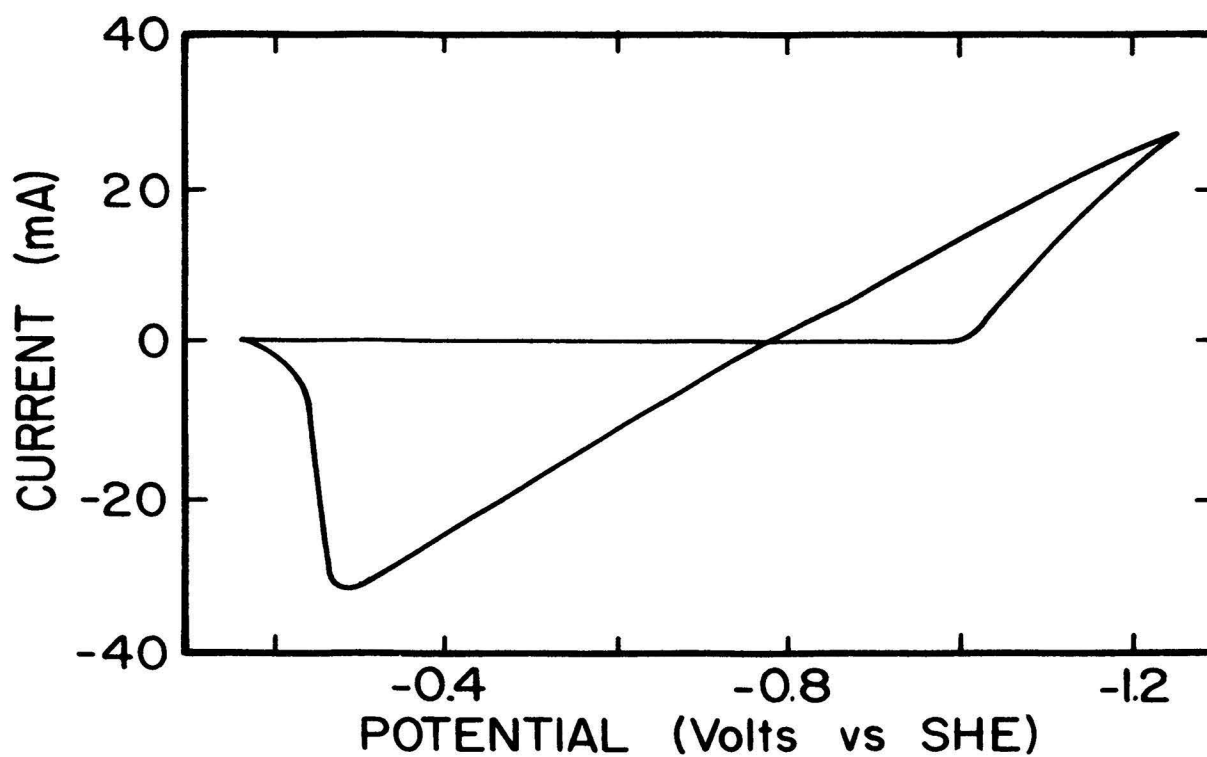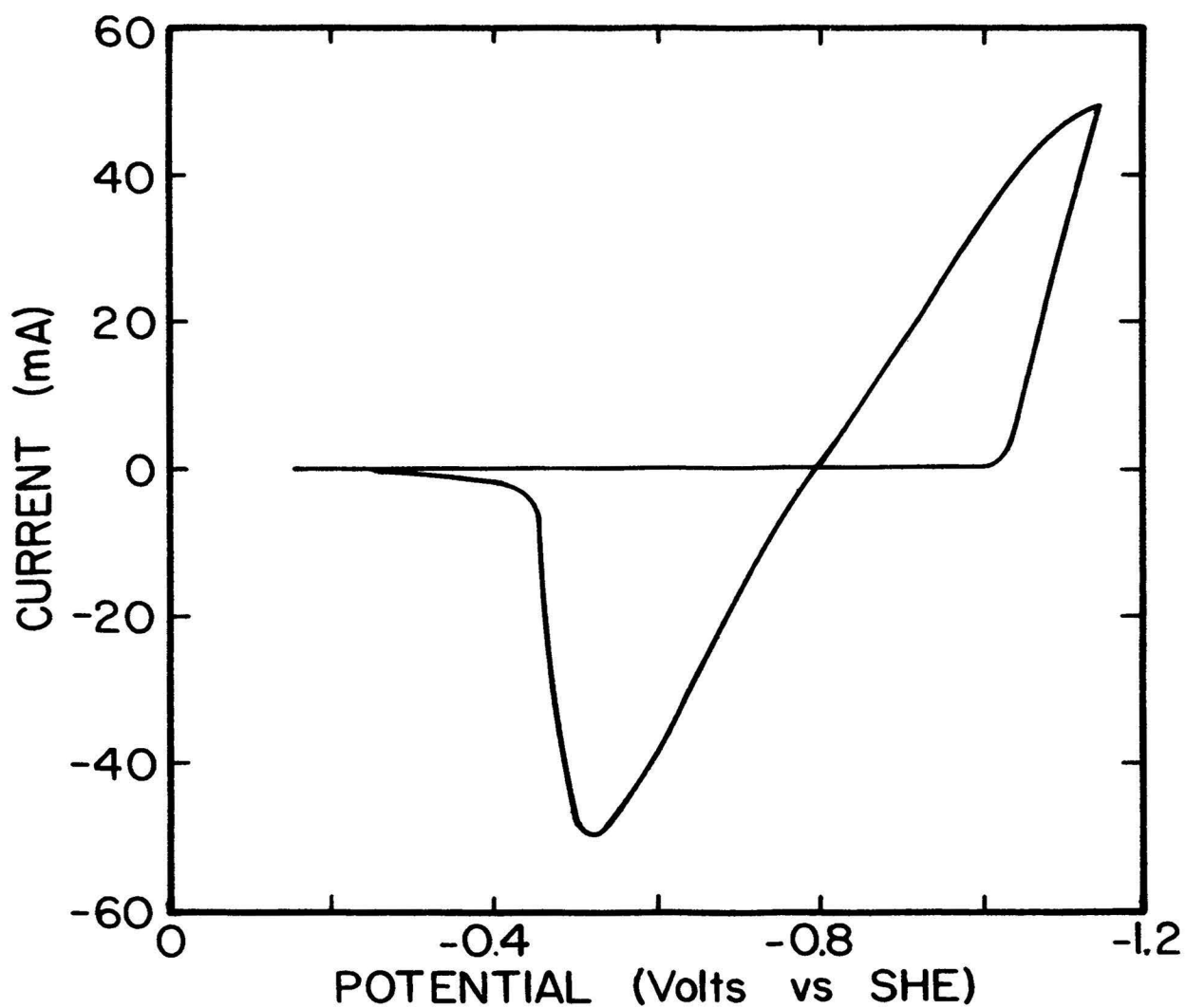aluminum cathode = 1.18 cm^2.
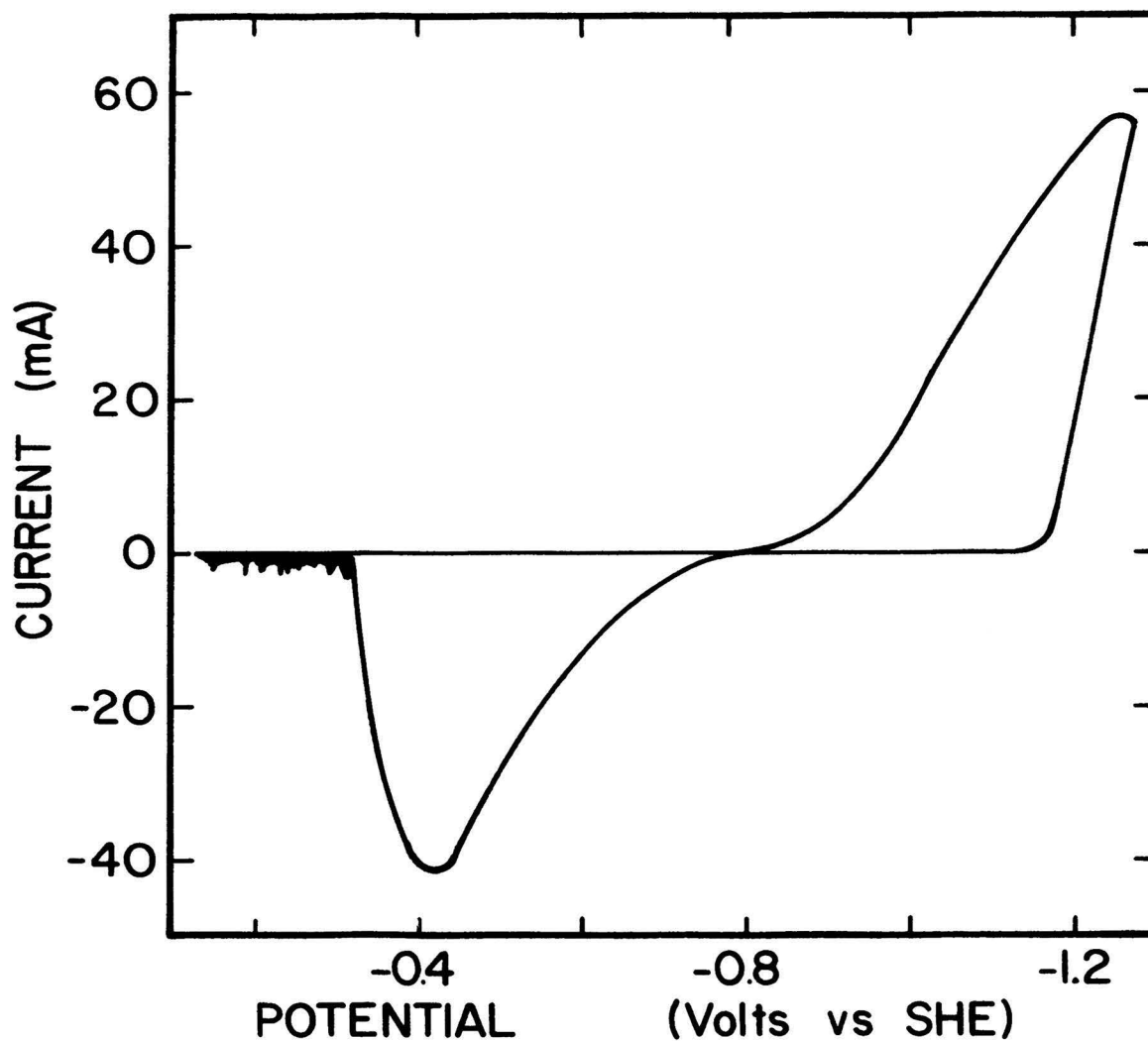
FIGURE 6. CYCLIC VOLTAMMOGRAM FOR ACIDIFIED ZINC SULFATE
ELECTROLYTE (0.77 M Zn^{++}, 1 M H_2SO_4) CONTAINING
40 ppm glue. Area of aluminum cathode = 1.18
cm^2.

the concentration for the particular plot shown. These curves showed increased polarization and higher values of decomposition potential, the degree of which was proportional to the concentration of glue added. Readily detectable changes in overpotential are produced for variations in concentration of 5-10 ppm, as can be seen in Figure 7. Cathodic potentials of 50, 62, and 74 mV at 10 ma cathodic current on the cathodic sweep (ABC) resulted with additions of 10, 20, and 40 ppm glue respectively. The average overpotential change occurring between 10 ppm and 20 ppm and that between 20 ppm and 40 ppm glue solution on the cathodic sweep were nearly identical. This shows that a doubling of glue concentration, in the ranges considered, produces an average potential increase of about 12 mV. Even though the cathodic curves are shifted with increasing glue addition, the relative slopes remain constant.

Another distinct characteristic of glue type curves was the asymptotic approach to crossover (portion C to D). An expanded scale view of this result is shown in Figure 8. The magnitude of this feature was also directly dependent on the glue content. The relative slope of the anodic current portion of the voltammogram appeared skewed for glue additions as compared to the fairly uniform or symmetrical shape obtained from pure solutions.

FIGURE 7.   POLARIZATION CURVES FOR ABC PORTION OF VOLTAMMOGRAM FOR ACIDIFIED ZINC
SULFATE ELECTROLYTE $(0.77 \text{ M Zn}^{++}, 1 \text{ M H}_2SO_4)$. 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.
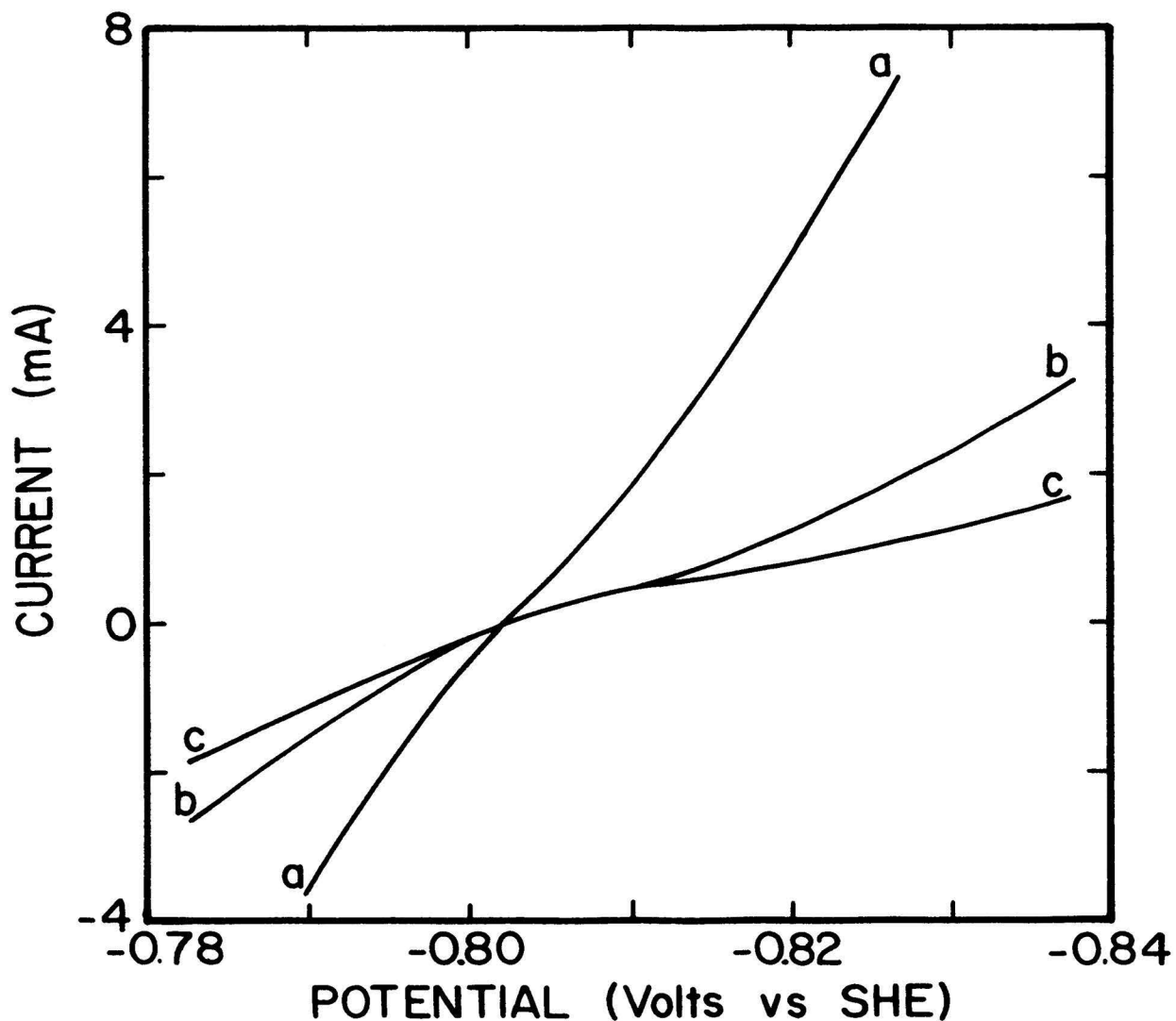
FIGURE 8. POLARIZATION CURVES FOR EXPANDED CD PORTION
OF VOLTAMMOGRAM PURE ACIDIFIED ZINC SULFATE
ELECTROLYTE (0.77 M Zn^{++}, 1 M H_2SO_4).
a, No additions and 10 ppb Sb; b, 10 ppm
glue; c, 40 ppm glue. Area of aluminum
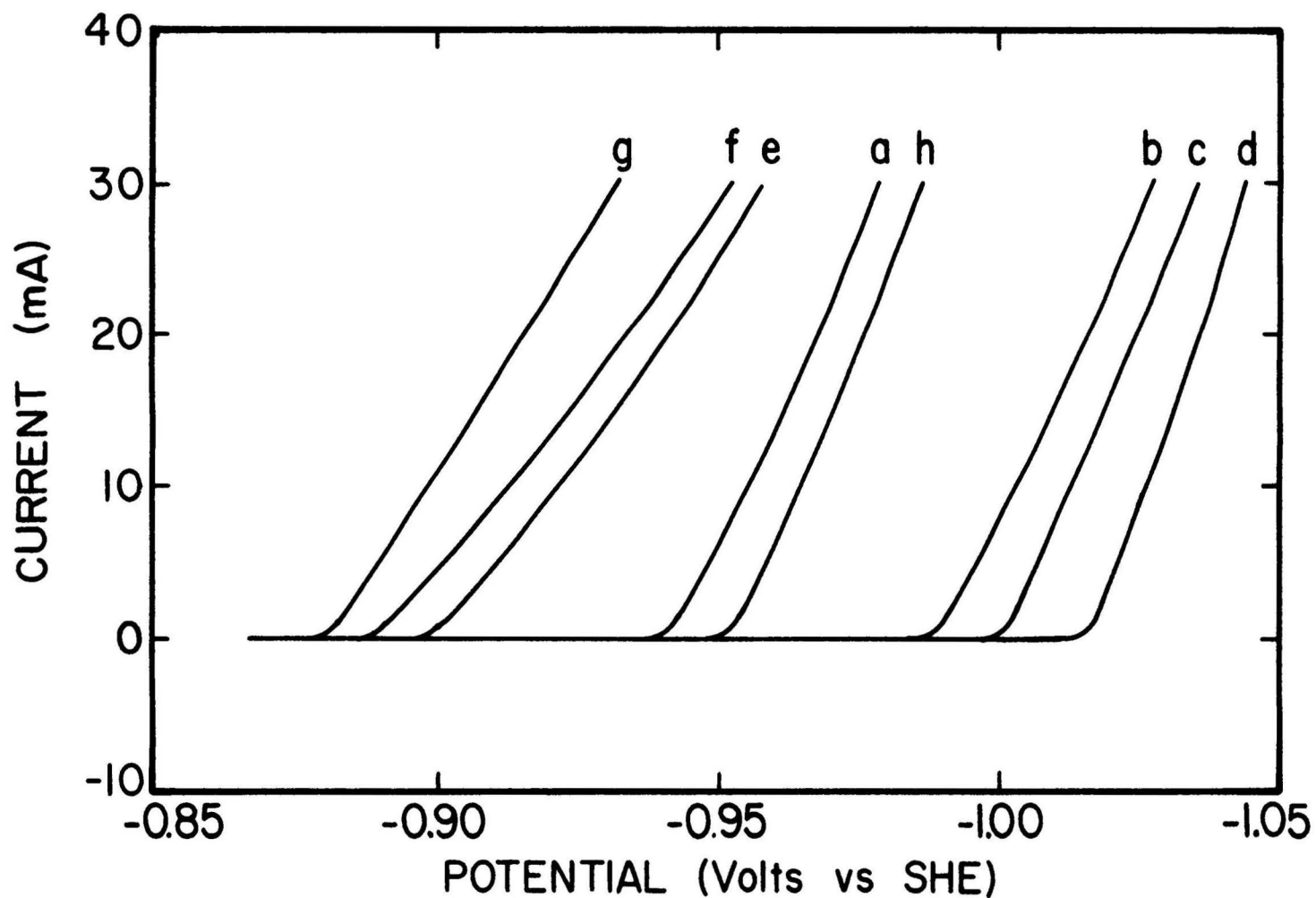cathode = 1.18 cm^2.

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. This was probably caused by the flakes intermittently resuming contact with the aluminum or general variations in the overall surface area of the zinc. The ratios of anodic to cathodic areas for glue additions were between 0.58 - 0.62, as compared to 0.83 for pure zinc electrolyte indicating a rather substantial decrease in efficiency. However, part of that was due to the incomplete anodic stripping previously discussed.

The amount of hydrogen which could be directly observed evolving from the cathode also seemed to be directly proportional to the quantity of glue in the solution. More specific and precise measurements would have to be made to verify this relationship.

Antimony Additions

When antimony was added to the acidified zinc sulfate electrolyte, a voltammogram typical to that shown in Figure 9 was obtained. The concentration of Sb for the voltammogram shown was 40 ppb. Antimony additions caused an effect opposite to that resulting from glue additions,
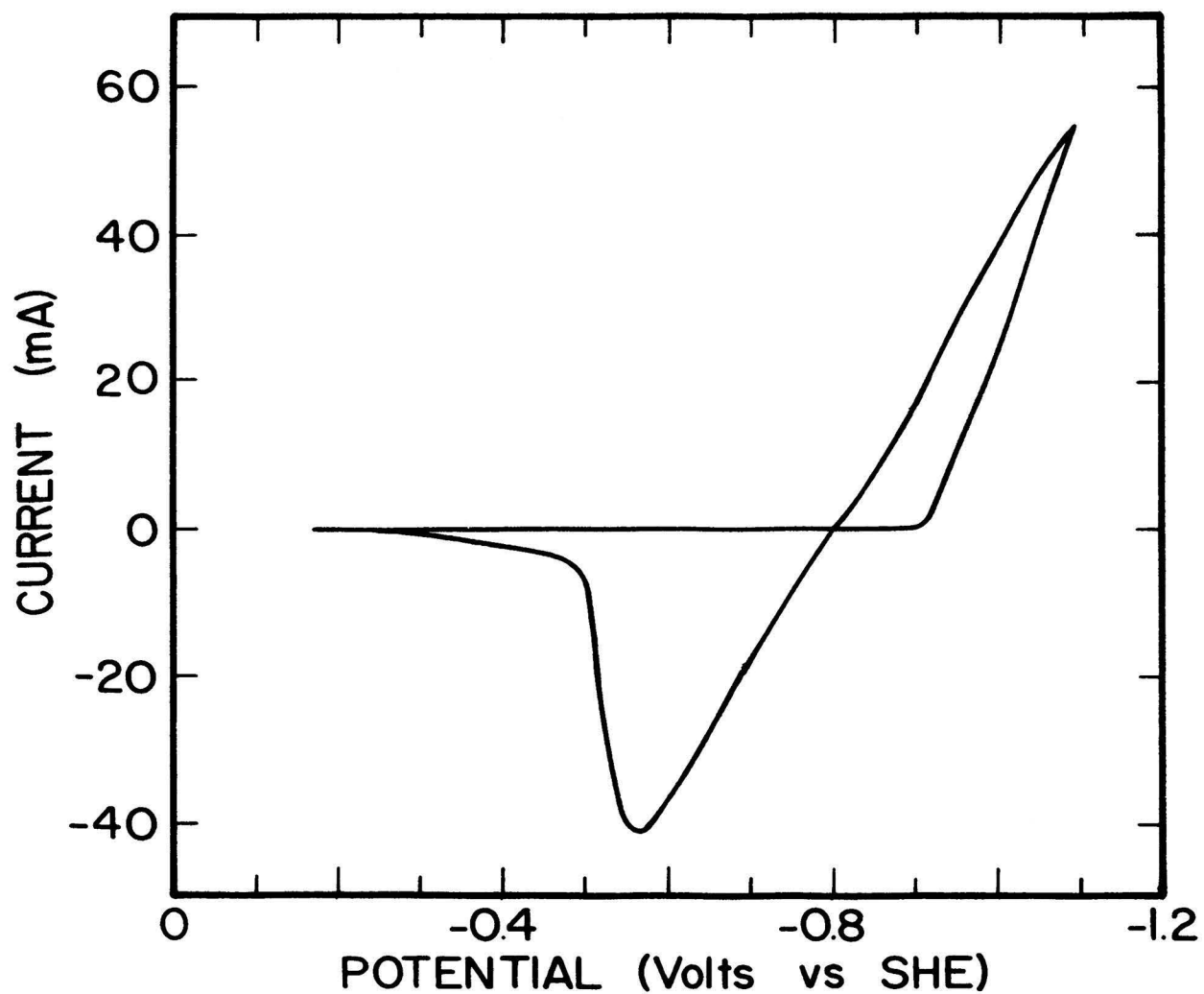
FIGURE 9, CYCLIC VOLTAMMOGRAM FOR ACIDIFIED ZINC SULFATE ELECTROLYTE $(0.77\ M\ Zn^{++},\ 1\ M\ H_2SO_4)$ CONTAINING 40 ppb Sb. Area of aluminum cathode = 1.18 cm^2.

in that a marked depolarization occurred. Changes in concentration as low as 5-10 ppb Sb can be detected by overvoltage differences, as can be seen in Figure 7. The decrease in overpotential was directly proportional to the concentration of antimony. A 43 mV decrease in the decomposition potential occurs for those solutions containing 10 ppb Sb as compared to pure zinc electrolytes. No significant characteristic behavior resulted as cross-over was approached (portion C-D) 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 area but they would most likely occur at lower currents, possibly in the microamp range.

The ratios of anodic to cathodic areas were 0.73, 0.57 and 0.61 for 10, 20 and 40 ppb Sb additions respectively, indicating a possible decrease in current efficiencies with increasing Sb. With 40 ppb Sb present, a noticeable amount of hydrogen could be seen evolving from the aluminum surface as completion of the cycle was approached.

Glue and Antimony Additions

Since Sb and glue additions produced opposite effects on the polarization curves and these reagents are also

used industrially to counteract each other, studies were also made of solutions containing various ratios of the two. 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 Figure 10. 40 ppb Sb and 20 ppm glue were the concentrations for the particular plot shown. 40 ppb Sb with 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 shown, but the combination of 40 ppb Sb with 10 ppm glue gave about the same characteristics as the pure electrolyte. Similar ratios, 40-80 ppb Sb to 15-30 ppm glue, were obtained in another study (6) in which cathodic efficiencies were obtained for various glue and antimony additions. It was noted for mixed additions, even with the proper ratio of additions 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 C-D) and the anodic current portion is skewed, similar to that for glue additions. The anodic to cathodic area ratios for glue and antimony mixtures averaged about 0.75, which is intermediate between those for pure zinc electrolyte and single impurity additions.
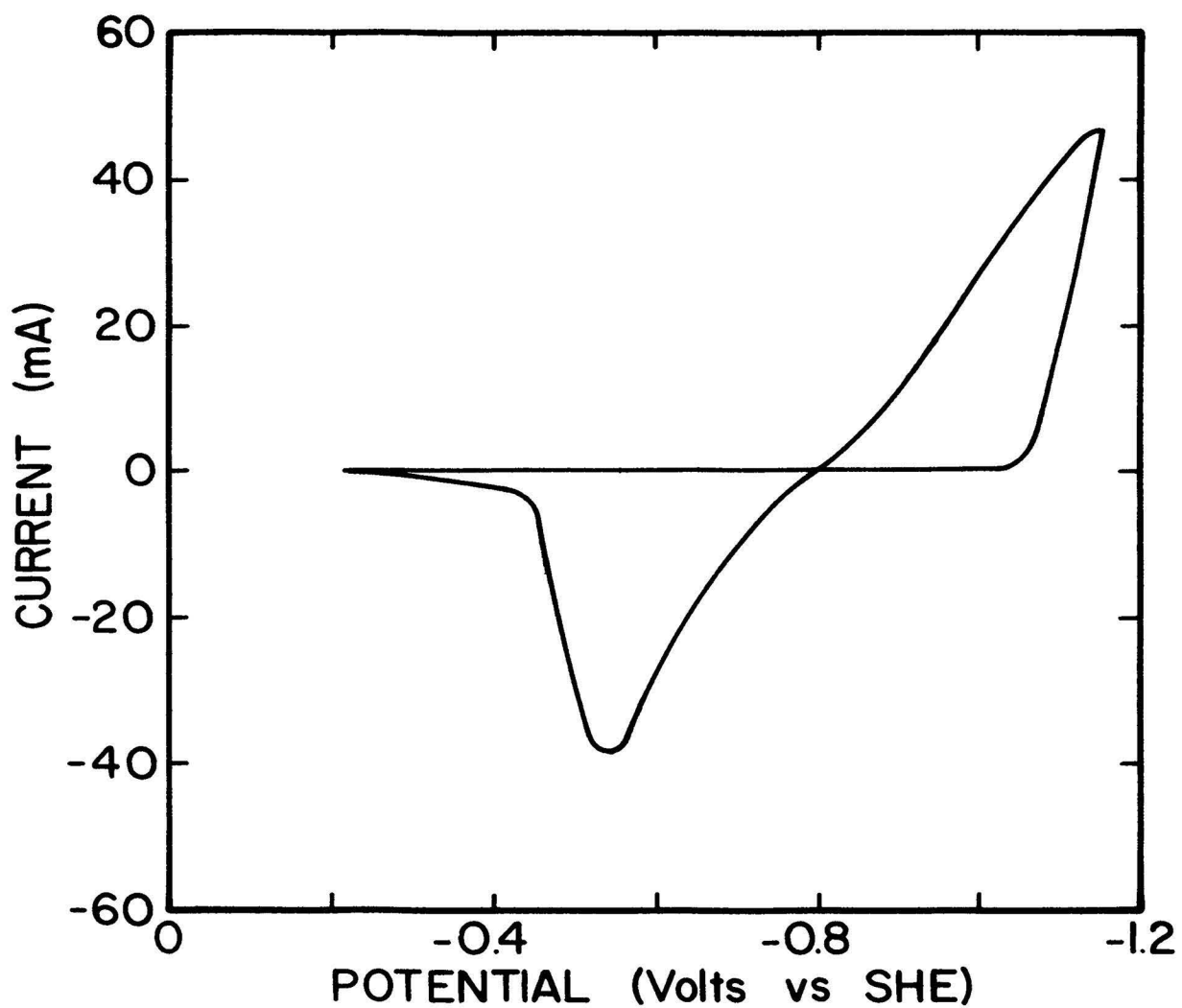
FIGURE 10.   CYCLIC VOLTAMMOGRAM FOR ACIDIFIED ZINC SULFATE
ELECTROLYTE (0.77 M Zn^{++}, 1 M H_2SO_4) CONTAINING
40 ppb Sb - 20 ppm glue.   Area of aluminum
cathode = 1.18 cm².

Cycle Variations

The effect of sweep rate on the characteristics of the voltammograms was studied for pure acidified zinc electrolytes. Sweep rates in the range of 1-100 mV/sec were examined. A decrease in current levels was noted for all sweep rates in this range, as seen in Figure 11. An inverse relationship resulted when comparing sweep rates with the ratio of anodic to cathodic curve areas as shown in Table II. An interesting result occurred for consecutive cycling at 1 mV/sec. The decomposition potential decreased with each succeeding cycle until the curves began to be reproducible after 5-6 cycles. The variation was most marked between the first and second cycles and the rate of change decreased with each cycle. This is probably due to incomplete stripping of the zinc during the anodic sweep since small zinc particles were detected on the aluminum surface by SEM examination after one complete cycle.

Deposit Morphologies

The various deposit morphologies obtained from electrolyzing both pure zinc solutions and solutions containing Sb or glue additons were studied using the scanning electron microscope. The coverage was evenly distributed for pure zinc deposits with the average

FIGURE 11. EFFECT OF SWEEP RATE ON THE CATHODIC POLARIZATION CURVE (PORTION ABC) FOR ACIDIFIED ZINC SULFATE ELECTROLYTE. a, 1 mV/sec; b, 5 mV/sec; c, 10 mV/sec; d, 50 mV/sec; e, 100 mV/sec. Area of aluminum cathode = 1.18 cm^2.
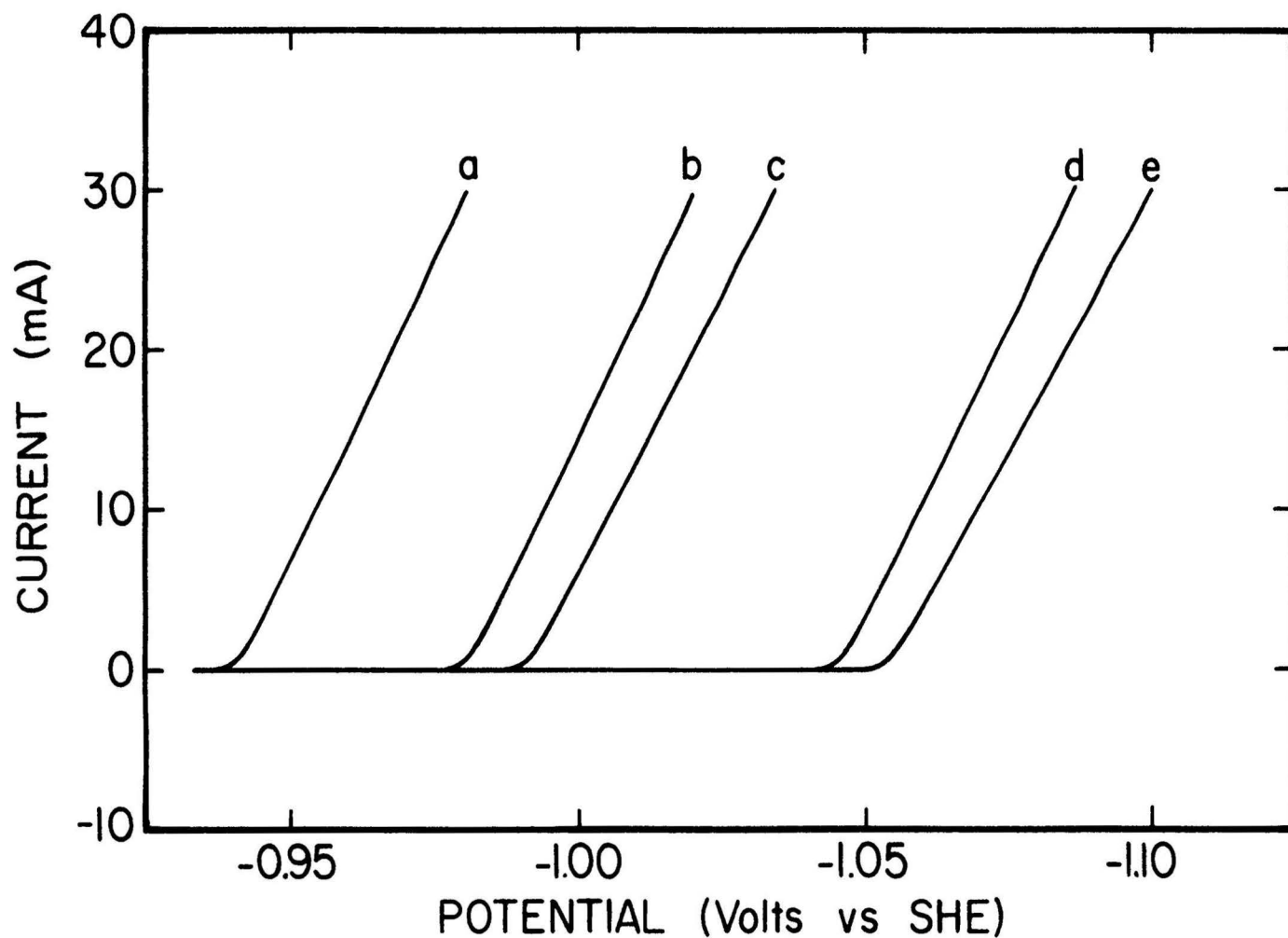
particle size being 5 μ as shown in Figure 12. Each crystal appeared to be growing independently of its neighbors with no tendency for the particles to join together. It is also evident that there was a substantial portion of the aluminum substrate which remains clear of any zinc, indicating a limited amount of initial nucleation. Deposits from Sb-containing solutions showed a marked increase in facet size (10 μ for 40 ppb Sb) and it was 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 was directly related to Sb concentration as shown in Figures 13 and 14. There was also no indication that corrosion was occurring, which is usually characterized by pits and irregularities in the facet edges. Glue addition deposits showed an average facet size of 1 μ with distinct preferred orientation characteristics, probably $(11\bar{2}0)$ (8), and the individual crystals (about 8 μ) tended to agglomerate more than those for pure zinc or Sb addition deposits. Each agglomerated "island" appeared to run parallel to the striations on the aluminum surface, which were produced in the polishing sequence as shown in Figures 15, 16 and 17. A slight glue excess morphology exists for the deposit containing 40 ppb Sb and 20 ppm glue additions.
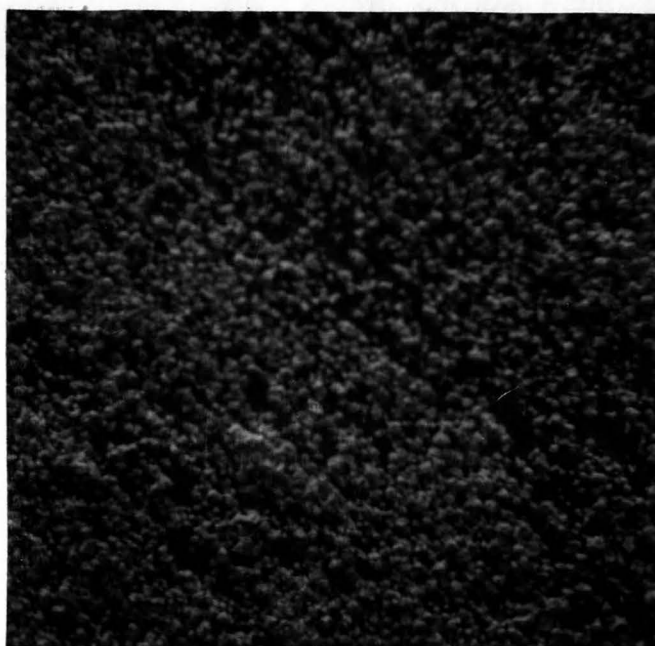
a
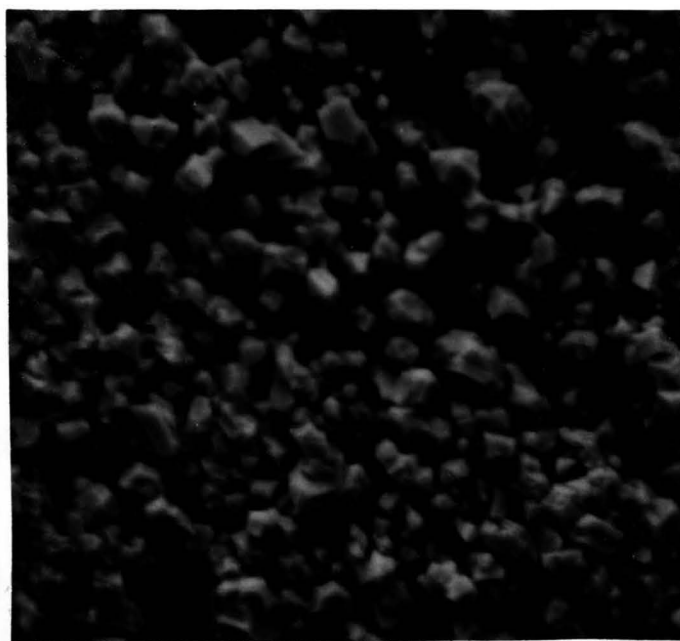
b

FIGURE 12. SCANNING-ELECTRON MICROGRAPHS FOR THE DEPOSIT
OBTAINED FROM ACIDIFIED ZINC SULFATE ELECTROLYTE
$(0.77 \text{ M } Zn^{++}, 1 \text{ M } H_2SO_4)$. a, 300×; b, 1000×.

FIGURE 13. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT OBTAINED FROM ACIDIFIED ZINC SULFATE ELECTROLYTE (0.77 M Zn^{++}, 1 M H_2SO_4) CONTAINING 10 ppb Sb, $1000\times$.

a

b

FIGURE 14.   SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT
OBTAINED FROM ACIDIFIED ZINC SULFATE ELECTROLYTE
(0.77 M Zn^{++}, 1 M H_2SO_4) CONTAINING 40 ppb Sb.
a, 300×; b, 1000×.

a

b

FIGURE 15.   SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT
OBTAINED FROM ACIDIFIED ZINC SULFATE ELECTROLYTE
$(0.77 \text{ M Zn}^{++}, 1 \text{ M H}_2\text{SO}_4)$ CONTAINING 10 ppm GLUE.
a, 300×; b, 1000×.

a
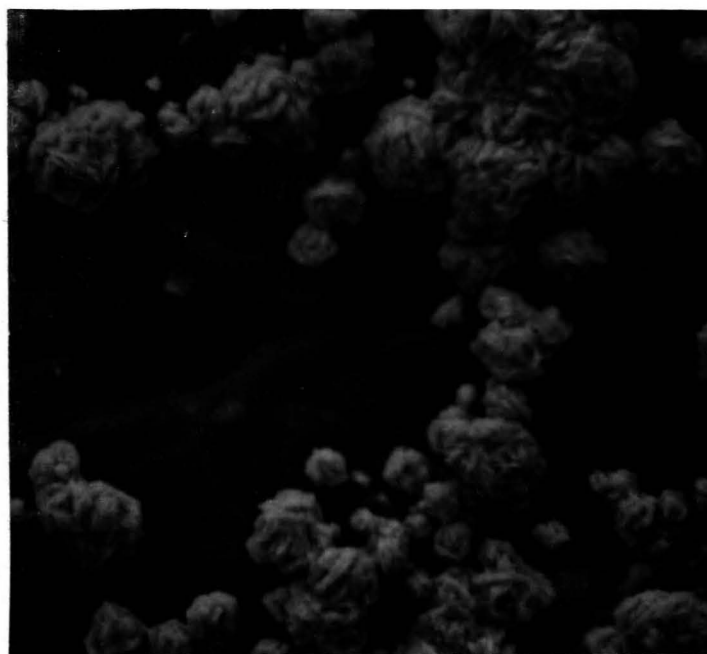
b

FIGURE 16.   SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT
OBTAINED FROM ACIDIFIED ZINC SULFATE ELECTROLYTE
$(0.77 \text{ M Zn}^{++}, 1 \text{ M H}_2\text{SO}_4)$ CONTAINING 40 ppm GLUE.
a, 300×; b, 1000×.

a
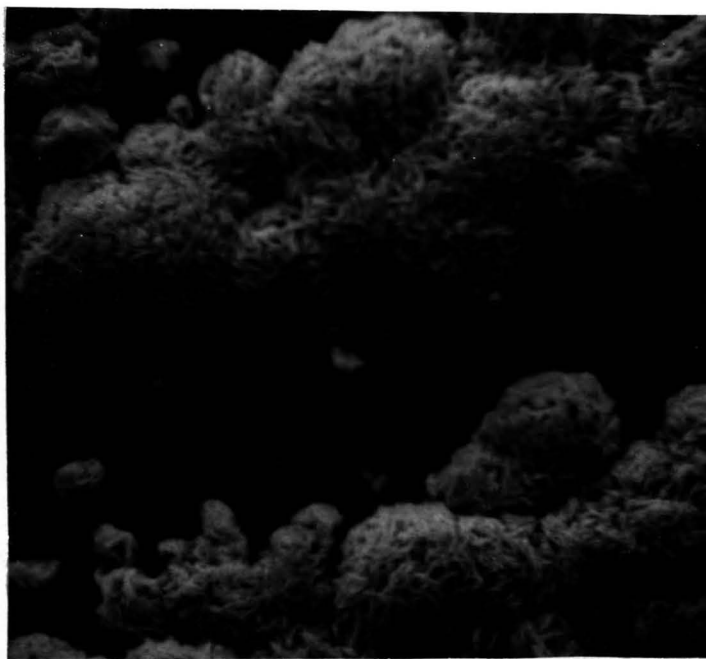
b

FIGURE 17. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT
OBTAINED FROM ACIDIFIED ZINC SULFATE ELECTROLYTE
$(0.77 \text{ M } Zn^{++}, 1 \text{ M } H_2SO_4)$ CONTAINING 80 ppm GLUE.
a, 300×; b, 1000×.

There appears to be substantial glue-like preferred orientation. However, the "islands" are more uniformly distributed over the aluminum cathode as shown in Figure 18.

Cu, Ag, and Ni Additions

A voltammogram representative of those obtained for Cu, Ag, and Ni additions is shown in Figure 19. 2 ppm Cu was the concentration for the plot shown. The most distinguishable features on these voltammograms were the slight cathodic peaks prior to the normal decomposition potential and also the substantial cathodic currents generated on the anodic sweeps (DEA) after all the zinc had been dissolved. These peaks were most probably produced by hydrogen because large amounts of gas could be seen evolving from the cathode. The magnitudes of these two peaks were directly proportional to the impurity concentration and the length of time the cathode was held in contact with the electrolyte. It was shown that Cu and Ag plated onto the aluminum substrate as these impurities were detected by nondispersive x-ray analysis EDAX and scanning electron microscopy. Micrographs and sample analyses are given in Figures 20 and 21. Ni could not be detected with the aid of EDAX and SEM analysis even though its presence was indicated by the shape of the curves.
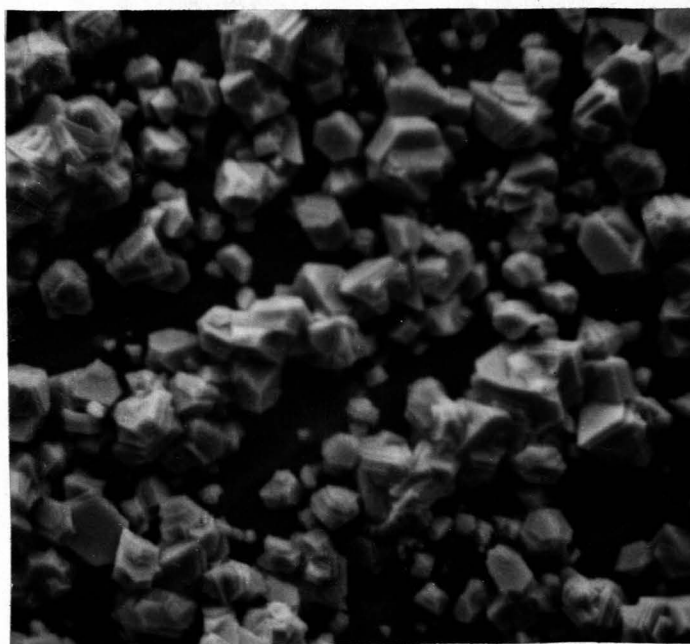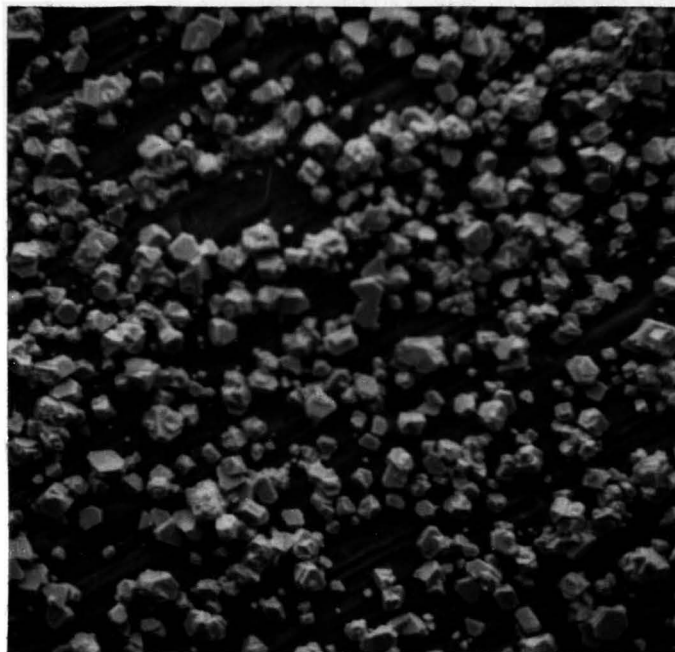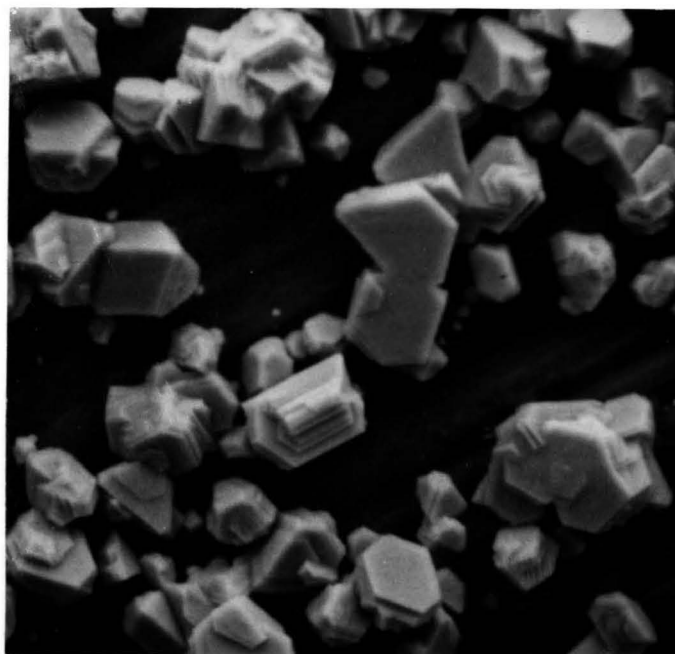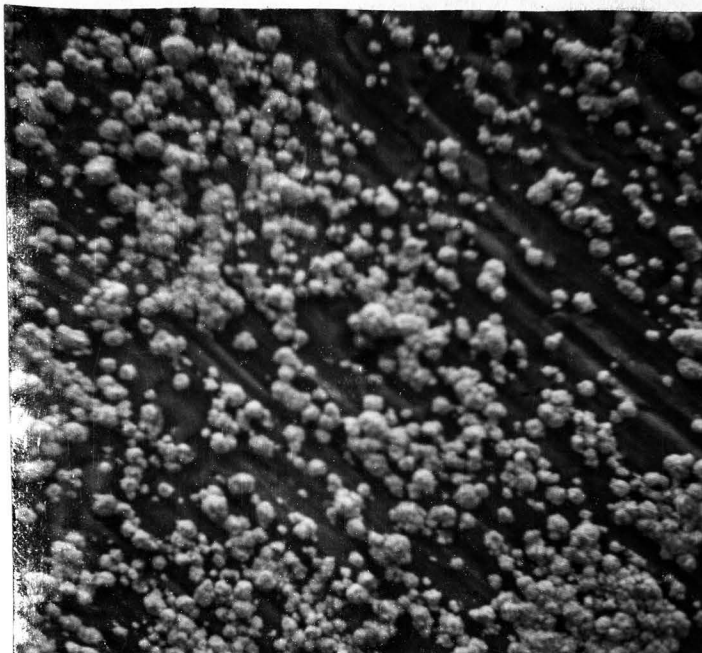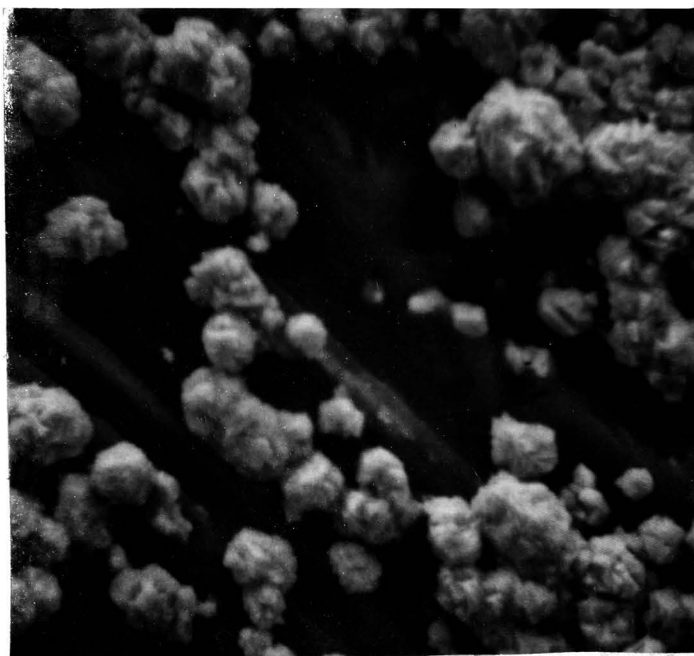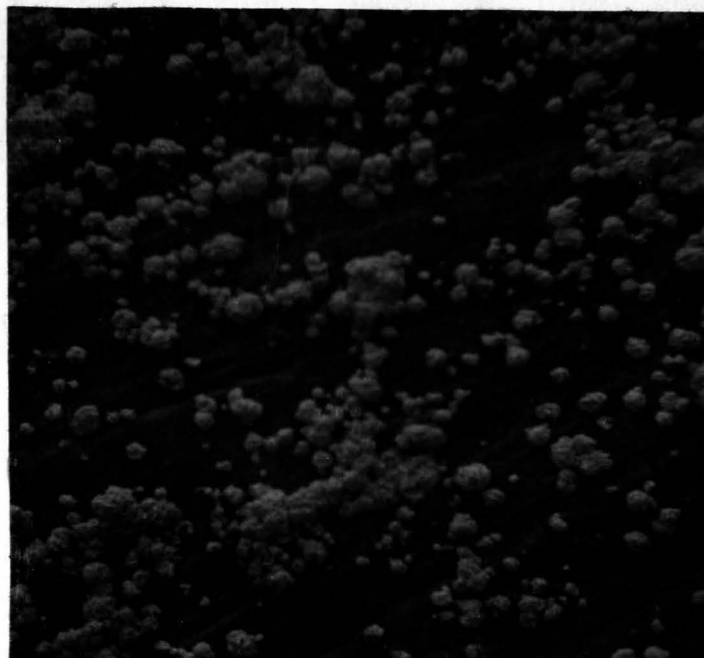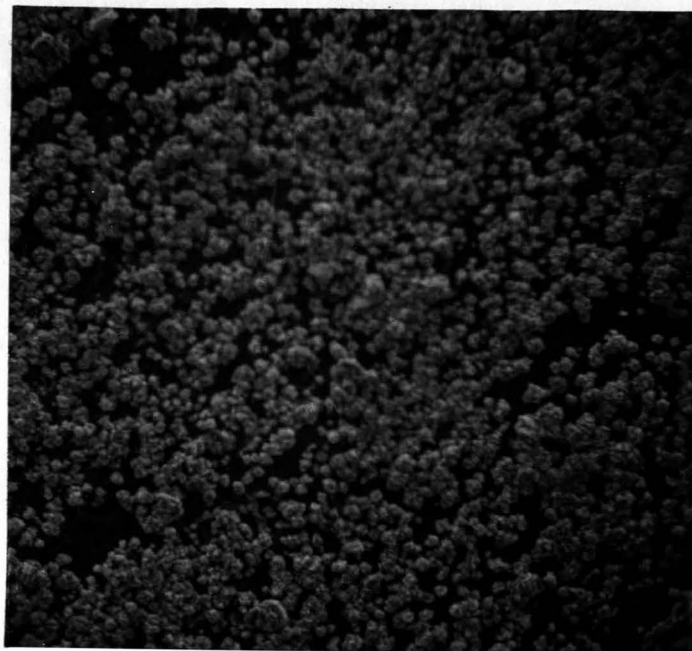
a
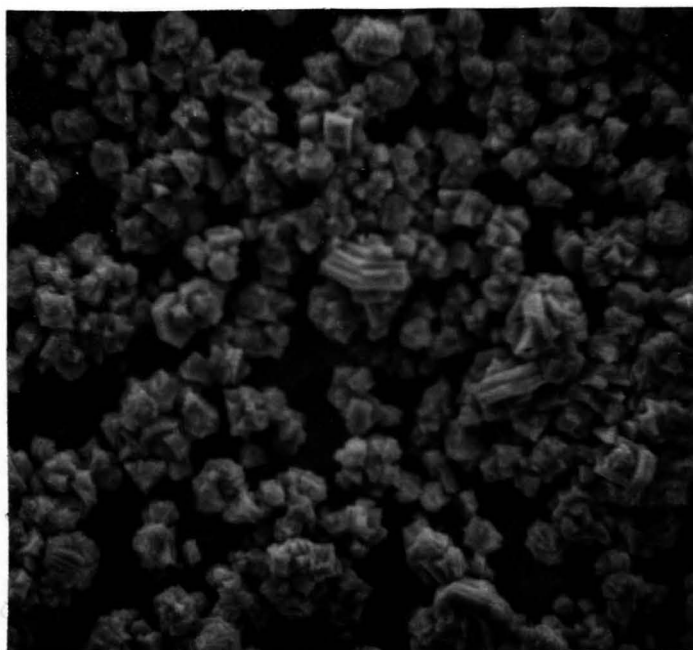
b

FIGURE 18. SCANNING-ELECTRON MICROGRAPH FOR THE DEPOSIT
OBTAINED FROM ACIDIFIED ZINC SULFATE ELECTROLYTE
(0.77 M Zn^{++}, 1 M H_2SO_4) CONTAINING 40 ppb Sb -
20 ppm GLUE. a, 300×; b, 1000×.
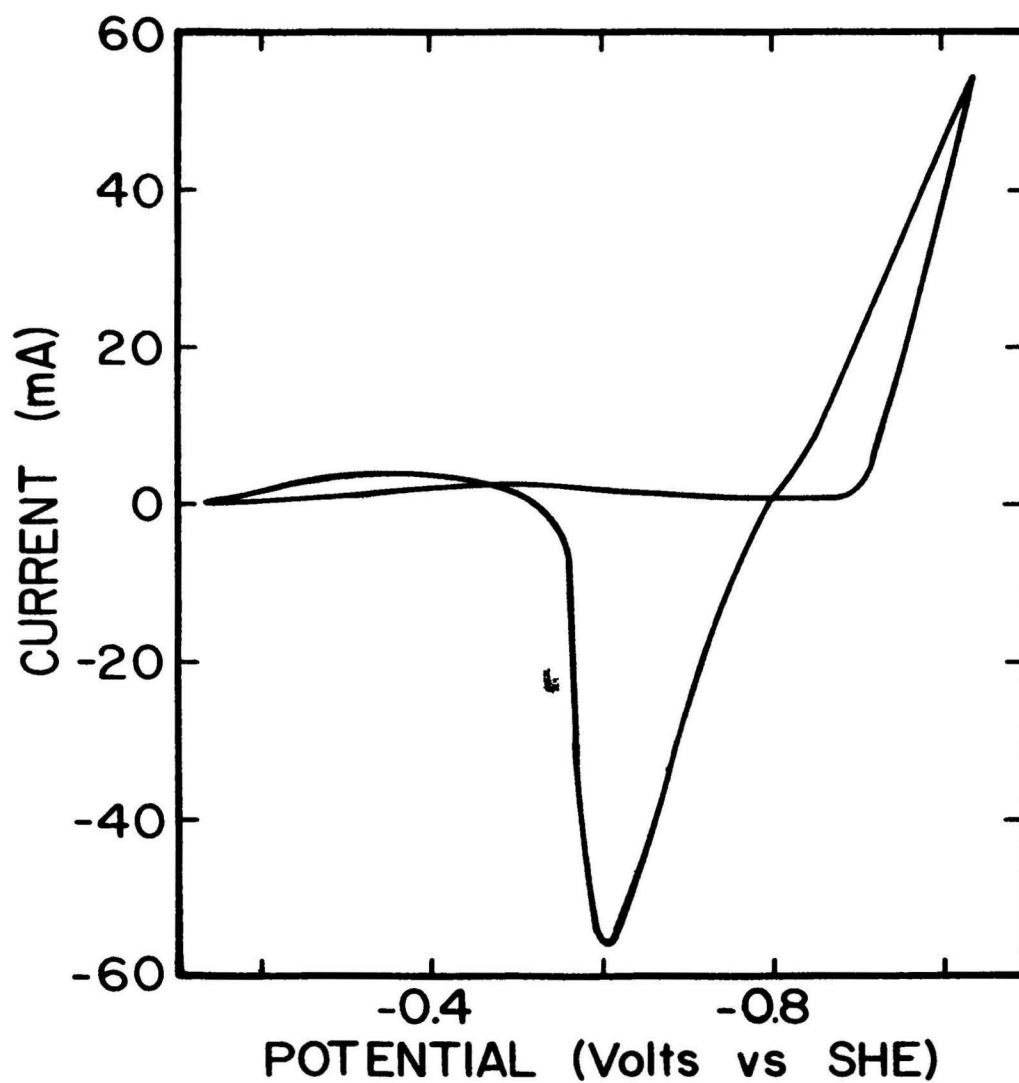
FIGURE 19.   CYCLIC VOLTAMMOGRAM FOR ACIDIFIED ZINC SULFATE
ELECTROLYTE (0.77 M Zn^{++}, 1 M H_2SO_4) CONTAINING
2 ppm Cu.   Area of aluminum cathode = 1.18 cm^2.

FIGURE 20.   SCANNING-ELECTRON MICROGRAPH SHOWING Cu
             DEPOSITED ON THE Al CATHODE.   Cu, 1000×.
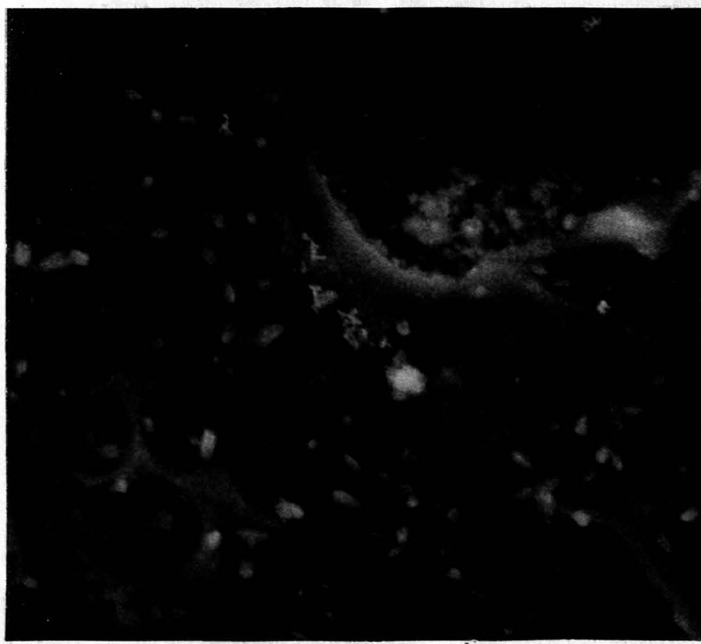
FIGURE 21.   SCANNING-ELECTRON MICROGRAPH SHOWING
             Ag DEPOSITED ON THE Al CATHODE.   Ag, 1000×.

DISCUSSION OF RESULTS

The results given previously show conclusively that the voltammetry technique used in this work is highly sensitive to the presence of various types of impurities or additives in zinc sulfate electrolyte. It also appears that testing of this type should allow not only an evaluation of the quality of the electrolyte but also will lend some insight into the specific type of impurity present. Aside from the valuable, practical information generated, this method also should allow a better understanding of the more basic aspects of the behavior of additives in zinc electrolysis.

Cycles should probably be run on at least a day-to-day basis to evaluate electrolyte efficiency on a commercial basis. One of the more important aspects of this technique is that it provides more than the usual "go" or "no-go" type testing. It should now be possible to create an internal standard for electrolyte quality and predict the causes of deviation from this norm by analysis of the polarization behavior. The advantage of this evaluation is that the relative or active organic concentration in solution can be estimated to a fair degree of accuracy. In the past it has been all but impossible to determine this parameter, which makes

cathode deposit control difficult at best. This technique could possibly be used as a short cut method to determine whether a newly developed leaching or purification process is giving good electrolysis without having to make extensive long-time deposits to determine cathode efficiency. It is also proposed that this tool can be used to evaluate different types of aluminum cathode blanks. It is reported that the aluminum cathodes behave differently depending on chemistry and process conditions. By employing different types of Al for the cathode and keeping the electrolyte composition constant, certain changes in the initial curve (portion ABC) might indicate certain desirable characteristics to prevent sticking, minimize poor adherence, or show improved corrosion resistance.

When an impurity is added to the pure zinc solutions, it can affect the deposition mechanism in two major ways. The impurity is likely to change the overpotential for zinc deposition or the hydrogen overvoltage on the surface of the cathode. These two effects probably occur simultaneously. In the case of glue additions, both the zinc deposition and hydrogen overvoltages on aluminum are increased. This would account for the increased decomposition potential (portion ABC) for glue additions. It appears that glue increases the zinc deposition potential on previously deposited zinc as shown by the asymptotic

approach to crossover. This substantial deposition over-potential is due to the overvoltage required for the zinc to deposit through the glue adsorption layer (10) and therefore affects the charge transfer rate. Glue also must increase the hydrogen overpotential, but to a lesser degree than the zinc overpotential because of the smaller ratio of anodic to cathodic curve areas and by the increased hydrogen observed evolving off the surface. Antimony, on the other hand, decreases the overpotential both for 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. The extent of these changes is not known at this time. Sb does not, however, appear to affect the deposition overpotential onto previously deposited zinc. This is surmised from noting that the approach to cross-over 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 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 Sb solution. The amount of Zn deposited, as evidenced by the anodic to cathodic area test, was small for the pure solution but there was absolutely no indication of any

Zn deposition with the Sb solution. Thus, it might be inferred that at lower current densities the Sb either enhances the hydrogen reduction reaction or causes any Zn that is deposited to redissolve or possibly both. It was shown that Sb had the tendency to give a low relative Zn plating efficiency, but it also seems that it has a greater influence on the hydrogen to zinc ratio at lower c.d. than at higher values when an Al cathode is used. Also, when an experiment was conducted in which a zinc cathode was substituted for the aluminum one, there was no difference noted in the initial part of the voltammogram obtained from the deposition of zinc, with or without a 40 ppb Sb addition. However there did seem to be a slightly higher (20%) current obtained with Sb at higher c.d.

It has long been recognized that hydrogen co-deposits with zinc. A correlation should be established between the relative amounts of zinc deposition and hydrogen evolution to the total cathodic current. In previous work by Cole (8), deposition of zinc with increased c.d. resulted in higher efficiencies. In view of this, it is imperative that when comparing the differences in the ratios of cathodic to anodic curve ratios to determine the relative efficiencies as affected by impurities, temperature, etc., the range should be controlled so as to always attain the same maximum current.

It is also known that hydrogen overvoltage on metals is directly proportional to c.d. (1). Therefore at the start of the scan where the c.d. is low, the proportion of hydrogen to Zn should be greater. This could be established by varying the potential scan range as described previously and comparing the ratios of the area under the curves to determine the relative proportion of zinc current to hydrogen current.

Previous studies (10) involving voltammetry and other techniques indicate that the deposition of zinc from zinc sulfate electrolytes is an irreversible process, or that the rate of charge transfer is relatively slow. The hydrogen evolution reaction, however, is a more reversible one (rapid charge transfer). Although no extensive evaluation of sweep rate was made in this study, for the limited ranges investigated, diffusion control has not been indicated since neither a limiting current nor any peaks were found. It was noted that the apparent zinc deposition efficiency (ratio of anodic to cathodic areas) decreased with increasing sweep rate. It is not too surprising to expect enhanced hydrogen evolution during the initial stages of polarization because of this basic difference in the reduction mechanism as compared to zinc. Because of this fact, considerable information could probably be gained by evaluation of the effect

of sweep rate on polarization as a function of various additives.

As was shown in the results, the morphologies obtained when glue was added were changed from those obtained with pure zinc electrolyte. One of the most noticeable effects was the apparent preferred orientation. It is known (8, 9) that certain facets and orientations are obtained under various process conditions and that the electrocrystallization is most influenced by c.d. and overpotential. When the Bravais law of crystal growth is obeyed, the most densly packed plane 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 could be expected to be more likely to grow by a lateral growth mode than an outward growth mode which would be more typical of higher overpotentials. The additions of glue caused 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 was 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. This also helps explain the reason that flakes of zinc fell off the aluminum surface during the anodic sweep when glue was present. The glue adsorption layer was so dense that the initial amount of nucleation was limited and occurred only on the raised portion of the striations which penetrated the adsorption layer. It has also been noted that cathodes containing high glue contents are more difficult to melt because of frothing, indicating inclusion of glue had taken place, which also strengthens the "bridging" assumption.

The morphology obtained with antimony additions was most marked by the large crystal facets which appeared to have a slight preferred orientation 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 adsorb on preferentially selected planes and inhibit zinc nucleation. The slower the nucleation rate the greater the crystal girth (9) which explains the increased facet size for antimony 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. This shows that the opposing influences of antimony and glue have both been active during the crystallization process.

The results showed that the copper, silver and nickel were deposited on the cathode and lowered the hydrogen overvoltage as indicated by the hydrogen evolution peaks. The magnitude of the peaks was indicative of the amount of impurity plated onto the aluminum surface which would be related to the area of deposited additive. The fact that the impurities plate onto the surface was verified by SEM and EDAX analysis.

In analyzing the results it must be kept in mind that the characteristics noted represent short time deposits and it can only be surmised what longer time deposits will show.

CONCLUSIONS

1. The cyclic voltammetry technique used in this work
    is highly sensitive in detecting various types of
    impurities or additives in zinc electrolytes.

2. Cathode material (Al, Zn, C, etc.) can influence
    the characteristics of the polarization curve for
    any given solution.

3. There is a quantitative relationship between decom-
    position potential and impurity concentration.

4. Changes in concentrations as low as 5-10 ppb Sb and
    5-10 ppm glue can be detected by overvoltage
    differences of about 20-40 mV.

5. Ratios of anodic to cathodic areas obtained from the
    curves can be used to approximate the relative zinc
    deposition efficiency.

6. The growth mode and morphology of zinc deposited from
    acidified zinc sulfate solutions is directly dependent
    upon type and concentration of impurity.

7. Antimony has a more pronounced effect on the deposi-
    tion of zinc on aluminum than on previously deposited
    zinc, causing impeded nucleation and enhanced
    hydrogen evolution.

8. Glue has a considerable effect on the deposition of zinc both on an aluminum surface and on previously deposited zinc and causes an outward mode of growth. Glue also causes agglomeration of the individual crystallites and acts as a nucleation agent, therefore keeping the facet size small (1 μ).

9. Future work should incorporate the effects of temperature, pH, sweep rate, potential range, cathode material, and other impurities on the characteristic voltammograms.

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VITA

Bruce Alan Lamping, was born on July 29, 1950 in Hackensack, New Jersey. He received his diploma from Indian Hills High School, Oakland, New Jersey in June 1968. From September 1968 to May 1972 he attended the University of Missouri - Rolla and received a Bachelor of Science Degree in Metallurgical Engineering in May 1972 and has been attending the Graduate School at the University of Missouri - Rolla since that time.

APPENDIX I
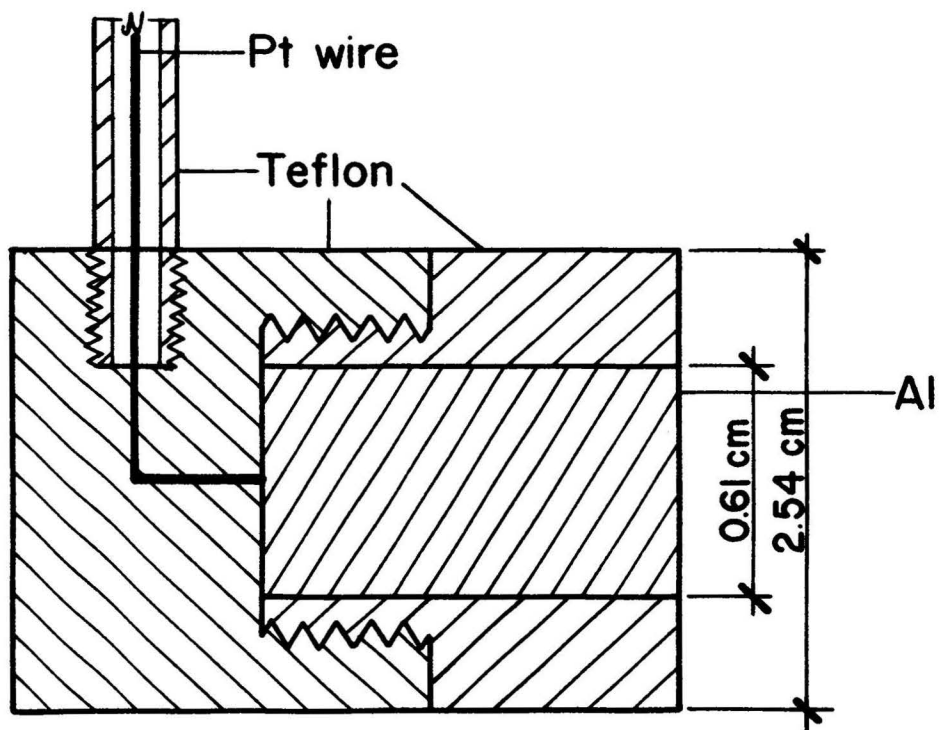
SCHEMATIC FOR ALUMINUM CATHODE

APPENDIX   II

COMINCO UNKNOWNS

Cominco Ltd. of Trail, B.C. had agreed to send six
solutions which they doped with various impurities to
serve as an unbiased evaluation of the technique
previously discussed.

All the samples had arrived frozen and a consider-
able amount of salt had precipitated from solution. The
containers of #5 and #6 samples were cracked and some of
the contents of these two had been lost causing a dilution
effect of unknown proportions. Each solution was evaluated
by performing a polarization experiment and ranking them
in order of increasing polarization, 5-3-4-1-2-6.
Electrolyte #4 appeared to be similar to the pure neutral
solution provided by Cominco Ltd for the majority of the
experimental work while solution #1 was similar to small
quantity of pure solution sent when the work first began
but was not used extensively. Since these two electrolytes
behaved differently, even though both had supposedly been
purified the same, there is a detectable difference between
neutral purified electrolytes. Based on closer scrutiny,
#4 was chosen to be neutral purified electrolyte, while
#3 appeared to be excess Sb(< 5 ppb). The latter

evaluation was based on the fact that the decomposition potential appeared to be rounded off and at the higher current values the cathodic curve crossed that for a pure solution. Also, the anodic area was less than for pure electrolyte. Electrolyte #5 appeared to have the highest Sb impurity content: probably a little less than 10 ppb. This decision was based upon an evaluation of its decreased polarization. Electrolyte #'s 1, 2 and 6 appeared to exhibit excess glue characteristics. This was concluded based on the assumption that #4 was the pure electrolyte. Number 1 appears to have contained about 5 ppm excess glue. It also seemed as though it might have been a mixture of antimony and glue since the anodic hump was shifted to the left. Number 2 and #6 appeared to contain excess glue, both in the range of somewhat less than 10 ppm glue. However, #2 appeared to have more glue than #6 if the slope at the crossover point was considered whereas #6 appeared to be more excess glue than #2 if the decomposition potential was considered. If antimony-glue mixtures were considered, #1 looked like about 20 ppb Sb and 10 ppm glue or 40 ppb Sb and 20 ppm glue. Number 2 would be expected to contain something like 40 ppb Sb and 30-35 ppm glue.

When the compositions of the six unknowns were obtained from Cominco Ltd the compositions were as

follows: #1 25 ppb Sb 15 ppm glue 5 ppb Ge. This should show a slight excess glue which was in agreement with the voltammogram. However, it was not really known exactly how Ge would affect the voltammograms. Number 2 actually had 40 ppm glue. This was appreciably more glue than had been predicted but the relation was correct in that excess glue was predicted by the voltammogram. Number 3 was 25 ppb Sb, 15 ppm glue. This should have shown a slight excess glue ~5 ppm however the voltammogram predicted a slight excess Sb. Number 4 was the neutral purified electrolyte which was predicted. Number 5 was 40 ppb Sb, this was in agreement with the prediction of being excess antimony but again the quantity was more than that assumed by evaluation of the voltammogram. Number 6 was 15 ppb Sb, 25 ppm glue which is considered excess glue. This is also in agreement with the prediction. In retrospect there were logical explanations for the small discrepancies obtained. One factor to be considered was the length of time the impurity was in contact with the zinc electrolyte. In the experimental work performed in this thesis, the impurity had contact with the zinc electrolyte for around half an hour. The impurities in the unknowns, however, had been in contact with the zinc throughout its entire shipment period and the solutions had been frozen for a considerable length of time during

shipment. Contents in #5 and #6 had leaked and, there-fore, the zinc concentration could have changed. All of the unknowns except #5 had a pH of about 4.85 with #5 having a pH of 4.61. This factor could have easily affected the resulting characteristics. A check was made on this premise by adding 40 ppm glue, the same as that used by Cominco for one solution, to #4 (neutral purified) and the results were comparable to those when 40 ppm glue was added to the starting solution used throughout the experimental work. This proved that either the effect of glue dissipated in the unknowns due to its extended contact with the electrolyte, or that there was a difference between the glue used in this paper and that which was supplied in the unknown.

It was generally agreed, after consultation with the staff at Cominco, that the technique had proven to be successful and from all indications cyclic voltam-metry is a viable method for the evaluation of at least zinc sulfate electrolytes and most probably others.