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The effect of germanium on zinc electrowinning from industrial acid sulphate electrolyte

D. J. MACKINNON, P. L. FENN

Metallurgical Chemistry Section, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Ontario, K1A 0G1, Canada

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The effect of germanium on the electrowinning of zinc from industrial acid sulphate electrolyte was studied using X-ray diffraction, scanning electron microscopy and cyclic voltammetry techniques. Germanium concentrations $> 0.1 \text{ mg l}^{-1}$ results in severe re-solution of the zinc deposit and hence decreased the zinc deposition current efficiency. Extreme fluctuations in the current efficiency occurred as a function of electrolysis time. Cyclic voltammograms obtained for Ge-containing electrolytes were characterized by a shoulder in the reverse scan prior to the cross-over potential. Vigorous hydrogen gassing occurred at the shoulder. These results are interpreted in terms of the formation of local Zn–Ge galvanic cells. Germanium concentrations to 0.2 mg l^{-1} had no effect on the morphology of the 1-h zinc deposits but the preferred orientation changed from [1 1 4] [1 1 2] for Ge-free electrolyte to [1 1 2] [1 1 0] for electrolytes containing Ge.

1. Introduction

The presence of impurities in zinc sulphate electrolyte decreases the current efficiency for zinc deposition, causing the total or partial dissolution of zinc during electrolysis and lowering the purity of the deposited zinc. The ease with which hydrogen ions can be reduced from solution in the presence of impurities is a critical factor. A time initiation effect and a synergism that occurs among the chemical species in solution are two complicating features that make it difficult to predict the extent of impurity effects on the current efficiency for zinc electrowinning.

Generally, there is not a uniform ratio of hydrogen to zinc partial currents throughout the electrolysis period. In fact, several investigators [1, 2] have reported that a cyclic deposition–dissolution phenomenon occurs for zinc electrowinning from impure electrolytes. Fosnacht and O'Keefe [1] recently observed that in the presence of cobalt and germanium, zinc did not deposit at a steady current for a given potential, but rather, cycles of zinc deposition and dissolution occurred. Zinc deposited initially, but, with time, vigorous hydrogen evolution began and very high current densities (200 mA cm^{-2}) were obtained. They interpreted these results in terms of the formation of local Zn–Co and Zn–Ge galvanic cells.

Maja *et al.* [2] observed that after a certain induction period the current efficiency (CE) obtained for zinc deposition from impurity-containing electrolytes abruptly decreased to zero and the zinc deposit dissolved in the electrolyte. When zinc dissolution was complete, a new deposit formed.

Fosnacht [3] reported that the current efficiency for zinc deposition decreased with increasing germanium in the concentration range $0–0.1 \text{ mg l}^{-1}$. Germanium showed significant interaction with glue; the addition of glue to an electrolyte containing germanium increased the current efficiency. Deposits electrowon at 430 A m^{-2} for 12 h from an electrolyte containing 65 g l^{-1} Zn + 100 g l^{-1} H_2SO_4 and 0.1 mg l^{-1} Ge exhibited highly preferred [0 0 2] [1 0 4] [1 0 2] orientations. Increasing amounts of glue added to this electrolyte changed the deposit orientation from [0 0 2] [1 0 4] to [1 0 1] [1 1 2]. Maja *et al.* [2] reported that zinc deposits electrowon from solutions containing Ge, Co or Ni had a morphology similar to that obtained for pure zinc

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deposits; the main difference was a reduction in grain size.

The present study was undertaken to examine the effects of Ge on the morphology and orientation of 1-h zinc deposits electrowon from industrial acid sulphate electrolyte under conditions normally applied in the zinc industry. The effect of Ge on zinc deposition current efficiency and the quantity of glue required to counteract the effect of Ge was also determined. Cyclic voltammetry experiments were conducted to characterize the effect of Ge on zinc deposition polarization.

2. Experimental procedure

2.1. *Electrolyte and apparatus*

The electrolyte was an industrial zinc sulphate solution prepared from hot zinc dust purified neutral zinc electrolyte obtained from Cominco Ltd, Trail, British Columbia. The average analysis was in g l^{-1}: Zn 150, $MgSO_4$ 38, Mn 1.6; in mg l^{-1}: Cd 0.2, Sb 0.2, Co 0.3, Ge 0.01, Ni 0.1, Cu 0.1, Fe 0.9, Pb 0.2, Cl 80, F 3.

Cell solutions were prepared by adding H_2SO_4, redistilled water and impurities to the electrolyte to give final concentrations of 55 g l^{-1} Zn and 150 g l^{-1} H_2SO_4. Animal glue was added as a concentrated solution. Germanium was added as germanium oxide in dilute HCl.

The electrolysis cell consisted of a 1 l beaker fitted with a Lucite cover which had slots cut in it to mount the electrodes [4]. A three electrode assemblage consisting of a central aluminium cathode and two platinum anodes was used. The cathode was fashioned from 4.7 mm thick Al sheet (purity 99.6%) obtained from Cominco. It measured 31.8 x 136.3 mm^2 and was mounted so that zinc deposited on both sides onto a total area of 12.9 cm^2. The anodes were cut from a 0.3 mm thick Pt sheet and measured 17.9 x 109.7 mm^2. The platinum anodes were used to avoid Pb contamination of the electrolyte from conventional Pb–Ag anodes [5].

2.2. *Electrolysis*

The electrolysis was run in a constant temperature bath at 35°C with stirring at a cathode current density of 430 A m^{-2} for a period of one hour. Additional tests were run at current densities of 323 and 215 A m^{-2} and for times up to four hours. Cathode conditioning was not emphasized for the electrodeposits and was carried out only when required.

2.3. *Examination of deposits*

Sections of the zinc deposits were examined by scanning electron microscopy to determine the surface morphology of the deposit and by X-ray diffraction to determine the preferred crystal orientation relative to the ASTM standard for zinc powder.

2.3. *Cyclic voltammetry*

Cyclic voltammograms were obtained using a voltage scan generator, a potentiostat and an x–y recorder for recording current vs applied potential plots. The voltage scan generator was used to cycle the potential from -0.7 to about -1.12 V vs a saturated calomel electrode. The latter limit being determined to give a maximum current of approximately 60 mA on the forward scan; hence there is some variation in the potential scan range. The scan was done at a rate of 1 or 2 mV s^{-1}.

The same cell was used for both the cyclic voltammetry and the electrowinning, however, the electrode assembly differed. The working electrode was an aluminium cathode measuring 15.4 mm x 109.5 mm x 0.8 mm thick. It was mounted so that the surface area was approximately 3.2 cm^2. The counter-electrode was one of the platinum anodes used in electrowinning. A saturated calomel electrode mounted adjacent to the cathode was used as the reference electrode.

Prior to each test the cathode was conditioned by polishing with 600 grit paper, washing the acetone followed by redistilled water, and patting dry with a tissue. The cathode was then put into the cell while the electrolyte was stirred. Once a steady rest potential was established, the stirrer was turned off and the scan was initiated.

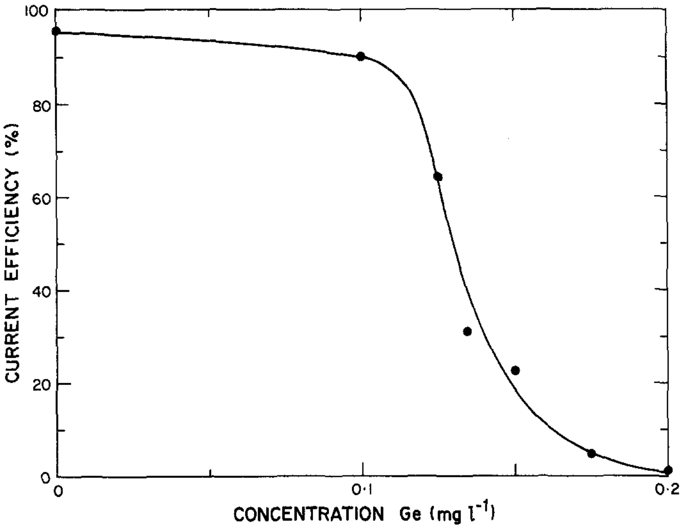

Fig. 1. Plot showing the effect of increasing germanium concentration on the current efficiency for 1-h zinc deposits.

3. Results and discussion

3.1. *Germanium effects*

3.1.1. Current efficiency. The effect of Ge on the CE for 1-h zinc deposits electrowon at 430 A m^{-2} is shown in Fig. 1. The CE decreased rapidly to very low values for Ge concentrations > 0.1 mg l^{-1} as a result of severe re-solution of the zinc deposit. The effect of various Ge concentrations on the 1-h zinc deposits is shown in Fig. 2. The three deposits shown in Fig. 2 were electrowon from solution containing 0.125, 0.135 and 0.150 mg l^{-1} Ge, respectively. As shown in Fig. 2, all three deposits indicate areas of extensive zinc re-solution. The re-solution (or corrosion) starts at the top-centre and gradually extends towards the sides and bottom of the deposit. The extent of this re-solution increases with increasing Ge concentration.

A series of experiments was performed to determine the effect of electrolysis time on the extent of Zn re-solution at a fixed Ge concentration. Zinc deposits were electrowon at 430 A m^{-2} from an electrolyte containing 0.15 mg l^{-1} Ge for periods of time ranging from 10 min to 4 h. The CE results are presented in Table 1. These data show extreme fluctuations in CE, particularly during the first hour of zinc deposition. The CE reached an average maximum (~ 89.5%) at time intervals of 15, 30 and 45 min, but at 60 min the CE was only 22.5%, thus ending the cycle; the CE obtained after 120 min was 53.4% and after 180 min was 23.2%; but after 240 min the CE decreased to 4.7%.

This behaviour suggests that the low CE obtained for electrolytes containing Ge is a result of re-solution of deposited Zn, together with a corresponding increase in hydrogen evolution. This phenomenon can be explained in terms of

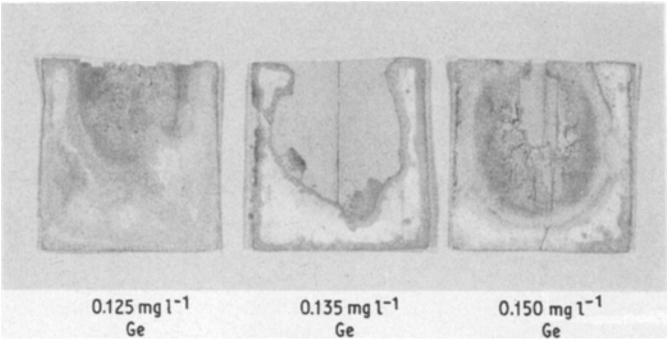

Fig. 2. Photographs of 1-h zinc deposits showing the effect of various germanium concentrations (magnification = ×1.2).

Table 1. The effect of electrolysis time on the current efficiency for Zn deposition from industrial acid sulphate electrolyte containing 0.15 mg l^{-1} Ge

Time (min)	*CE (%)*
10	45.5
15	90.0
20	25.8
25	21.9
30	86.8
35	7.3
40	22.8
45	91.7
50	81.4
55	21.0
60	22.5
120	53.4
180	23.2
240	4.7

Electrolysis conditions: 55 g l^{-1} Zn; 150 g l^{-1} H_2SO_4; 35°C; 430 A m^{-2}.

local Zn–Ge cell formation as suggested by Fosnacht and O'Keefe [1]. Co-deposition of Ge with Zn can provide sites of low hydrogen overvoltage. After some time, H_2 is evolved at these sites as zinc continues to deposit. The corresponding anodic reaction (to cathodic H_2 evolution) is the re-solution of Zn at sites adjacent to the low hydrogen overvoltage areas. As Zn dissolves, more impurity metal is exposed and both the rate of hydrogen evolution and Zn re-solution increase. Ultimately, Zn dissolves faster than it deposits and the result is a rapid decrease in the CE. When most of the zinc has redissolved, the rate of zinc deposition increases, the CE increases and the zinc deposition re-solution cycle begins again.

As indicated in Fig. 3, and in agreement with Fosnacht [3], the addition of glue to the electrolyte significantly improved the CE, for an electrolyte containing 0.135 mg l^{-1} Ge, the CE was optimized when 5 mg l^{-1} glue was added to the electrolyte. Fig. 4 shows the effect of increasing Ge concentration on the CE for 1-h zinc deposits electrowon from an electrolyte containing 10 mg l^{-1} glue. As indicated, there is a gradual decrease in CE with increasing Ge concentration.

3.1.2. Deposit morphology and orientation. Fig. 5 compares the morphology of the zinc deposits obtained from addition-free, germanium and (germanium + glue-containing electrolytes). Although Ge decreased the CE, its presence in the electrolyte had no significant effect on the morphology of the 1-h zinc deposits (see Fig. 5b) which is similar to that found for Zn electrowon from the addition-free electrolyte (see Fig. 5a). The morphology of the 1-h deposit electrowon from a solution containing 0.15 mg l^{-1} Ge + 15 mg l^{-1} glue (see Fig. 5c) was also similar to that observed for Zn electrowon from the addition-free solution (see Fig. 5a). Thus, the morphology of these 1-h deposits was similar to that obtained by

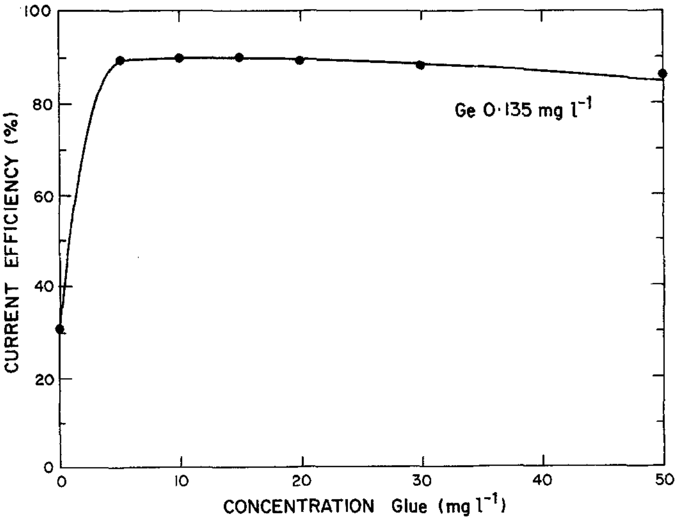

Fig. 3. Plot showing the effect of increasing glue concentration in the presence of germanium on the current efficiency for 1-h zinc deposits.

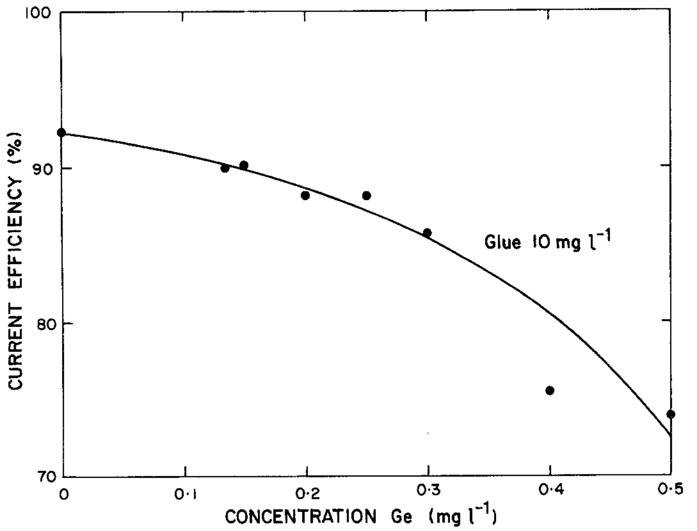

Fig. 4. Plot showing the effect of increasing germanium concentration in the presence of glue on the current efficiency for 1-h zinc deposits.

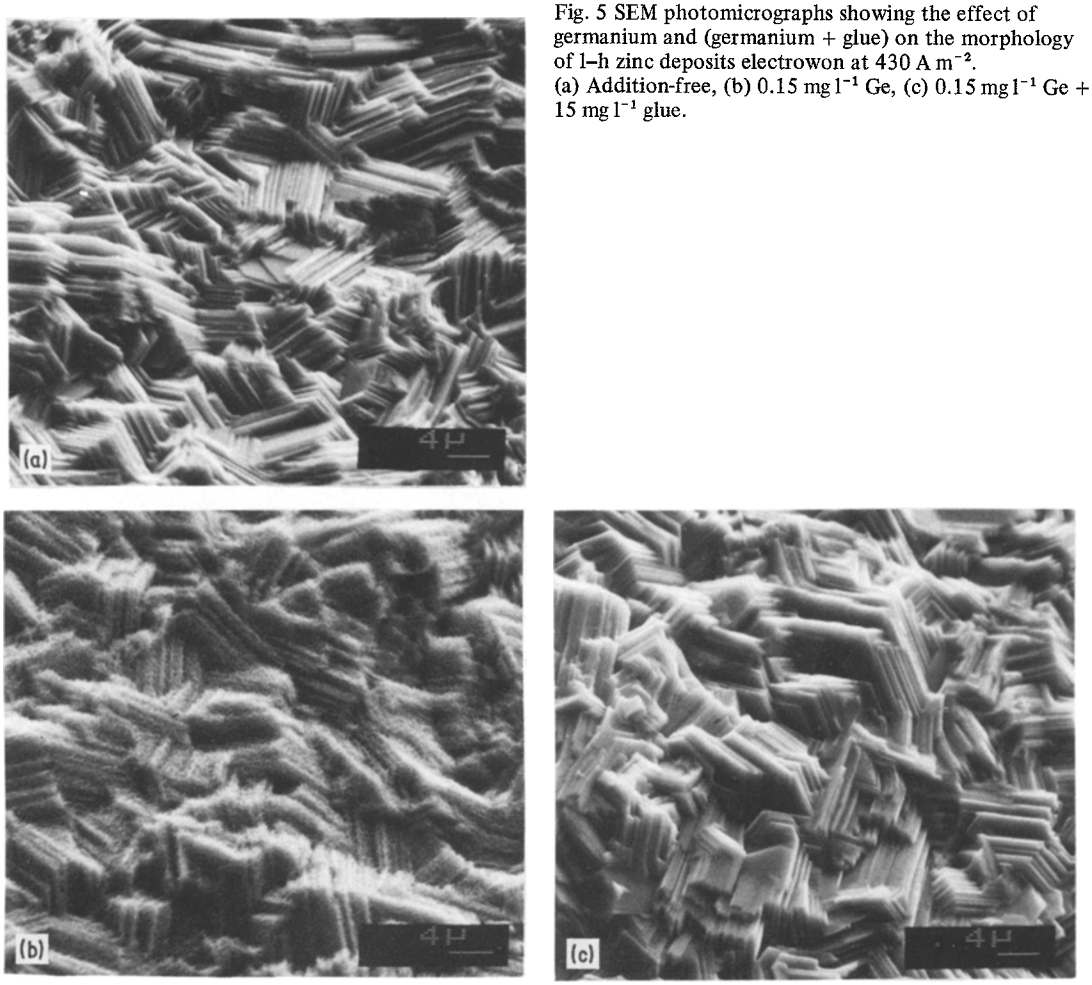

Fig. 5 SEM photomicrographs showing the effect of germanium and (germanium + glue) on the morphology of 1-h zinc deposits electrowon at 430 A m^{-2}.
(a) Addition-free, (b) 0.15 mg l^{-1} Ge, (c) 0.15 mg l^{-1} Ge + 15 mg l^{-1} glue.

Maja *et al.* [2], but different from that obtained by Fosnacht [3]. However, the difference may be related to the different experimental conditions employed by Fosnacht [3]; namely, 65 g l^{-1} Zn, 100 g l^{-1} H_2SO_4, 0.01–0.1 mg l^{-1} Ge, 45°C for 12 h. The preferred orientations for the 1-h Zn deposit electrowon from Ge-containing electrolyte was [1 1 2]; however, unlike the addition-free deposit [4] it showed a significant [1 1 0] component.

3.1.3. Polarization. Cyclic voltammetry is a convenient technique for measuring zinc deposition polarization effects. In this technique a controlled potential is applied to an electrolysis cell and the resulting current is displayed against the applied potential. A typical voltammogram obtained for zinc deposition from an addition-free electrolyte is shown in Fig. 6. The initial potential sweep is started at point A and the Curve AB is the initial decreasing voltage portion for which the applied potential is more positive than the zinc reversible potential; therefore, zinc deposition does not occur. The point B is the potential at which the Curve DE crosses the zero current line ('crossover potential') and approximates the zinc reversible potential for the solution being tested. The line BC corresponds to the activation overpotential associated with zinc deposition onto the Al cathode. The Curve CD represents the polarization overpotential associated with zinc deposition onto Al. At Point D, the applied potential is reversed. The Curve DB corresponds to the polarization overpotential associated with zinc deposition onto freshly deposited zinc. The Curve CDB in fact represents a non-steady-state condition in which the Al cathode is increasingly being covered by zinc; hence, the shape of the curve will vary depending on the voltage scan rate. The Curve BEA represents the anodic dissolution of the previously deposited zinc.

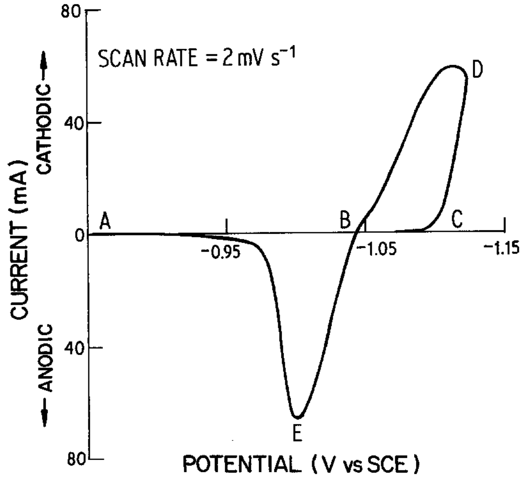

Fig. 6. Cyclic voltammogram obtained for addition-free inductrial acid zinc sulphate electrolyte. Scan rate = 2 mV s^{-1}.

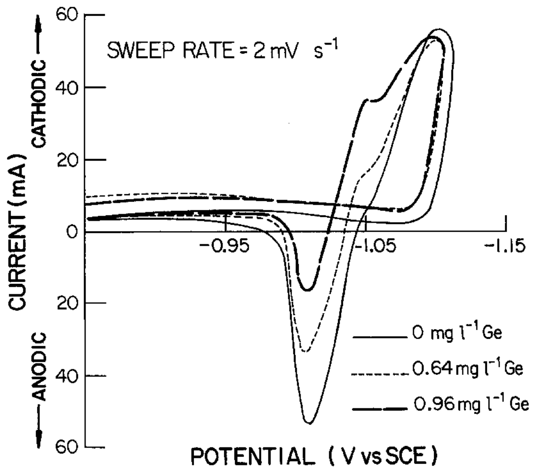

Fig. 7. Cyclic voltammograms showing the effect of germanium on zinc deposition polarization. Scan rate = 2 mV s^{-1}.

The voltammograms obtained for zinc deposition from electrolytes containing 0.64 and 0.96 mg l^{-1} Ge are compared to that for a Ge-free

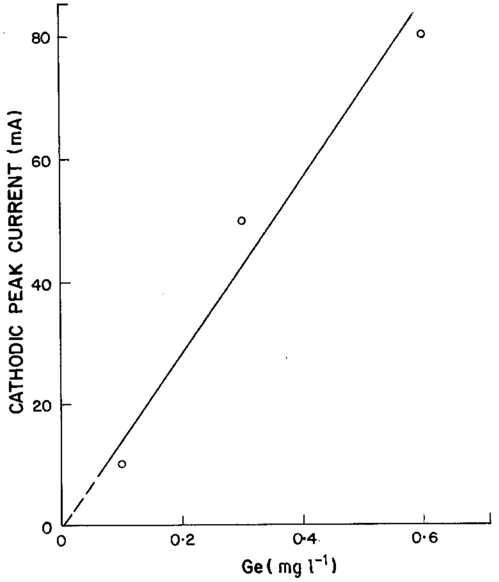

Fig. 8. Plot showing the correlation between cathodic current peak (see Fig. 7) and germanium concentration in the electrolyte.

electrolyte in Fig. 7. At 0.64 mg l^{-1} Ge, a shoulder appears in the reverse scan prior to the cross-over potential. At 0.94 mg l^{-1} Ge, the shoulder is more pronounced and occurs at a more negative potential. Vigorous H_2 evolution is observed at the electrode surface when the potential is in the region of the shoulder on the voltammogram.

The values of the cathodic currents associated with the shoulders in the voltammogram (see Fig. 7) are plotted vs Ge concentration in Fig. 8. The resulting plot is linear and in good agreement with a similar relationship obtained by Fosnacht and O'Keefe [1]. However, these latter authors obtained their voltammograms as log *I* vs *E* and thus were able to detect Ge levels as low as 0.02 mg l^{-1}. These results indicate that this polarization technique may be useful for determining the concentration of Ge in zinc electrolyte prior to electrowinning.

The phenomenon occurring at the shoulder region of the voltammogram (Fig. 7) was investigated in more detail (Fig. 9) for an electrolyte containing 0.6 mg l^{-1} Ge. As was the case in Fig. 7, a shoulder appears prior to the cross-over potential between −1.054 and −1.040 V vs SCE during the reverse scan (solid curve) (see Fig. 9). On completion of the first scan, a second scan was run (dashed curve). However, this time the scan was stopped at − 1.046 V vs SCE (Point a); i.e. midway on the shoulder during the reverse scan. The cathodic current increased rapidly from about 12 to 33 mA and then began to decrease. Vigorous gassing was observed during this time. At 28 mA the potential scan was re-started and the cycle was completed. However, only a small anodic peak was observed indicating that most of the deposited Zn had already dissolved while the potential was held at −1.046 V vs SCE.

A third scan was run in which the potential was held constant at −1.070 V vs SCE (Point b); i.e. prior to the potential region for the shoulder on the reverse scan. A slow increase in current occurred. The potential scan was resumed when the cathodic current reached 38 mA (Point b). Vigorous gassing was not observed while the potential was held constant; the shoulder occurred after the scan was resumed in the same potential region as for the previous curves. An increase in the anodic portion of the curve was also observed which indicates that Zn continued to deposit while the potential was held at − 1.07 V vs SCE.

The shoulder region of the cyclic voltammograms obtained for electrolytes containing Ge has been termed the 'instability region' [1, 2]. In this instability region, increased hydrogen evolution is observed as zinc dissolves. This behaviour suggests a local cell type of impurity interaction whereby germanium sites act as local cathodes and the adjacent zinc sites as local anodes.

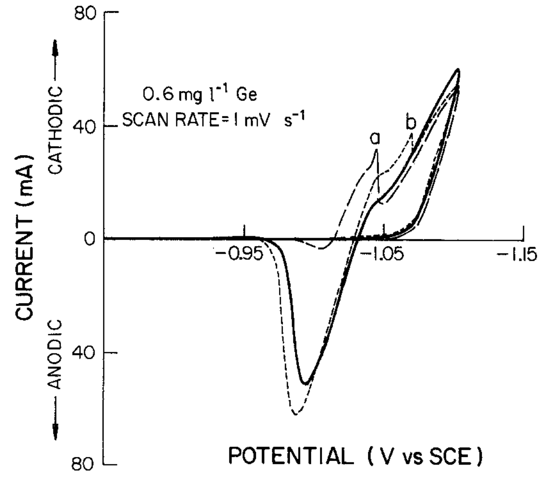

Fig. 9. Cyclic voltammograms showing the effect of germanium on zinc deposition polarization: (a) potential held at −1.046 V vs SCE; (b) potential held at −1.070 V vs SCE, scan rate = 1 mV s^{-1}.

4. Conclusions

The current efficiency for 1-h zinc deposits electrowon from industrial acid zinc sulphate electrolyte is adversely affected by concentrations of germanium > 0.1 mg l^{-1}. The presence of Ge in the electrolyte causes a rapid decrease in the CE, and severe re-solution of the 1-h zinc deposits. The presence of Ge also caused the CE to fluctuate between extremely low and high values during the 1-h electrolysis period. Ge had no effect on the morphology and only caused minor changes in the preferred orientation of the 1-h zinc deposits. The addition of glue to the electrolyte was found to counteract the effect of Ge to some extent.

The cyclic voltammograms for zinc deposition from electrolytes containing Ge were characterized by a shoulder region in the reverse scan prior to the cross-over potential. Vigorous hydrogen evolution and zinc re-solution were observed to occur at this shoulder region. This observation together with the cyclic behaviour of the CE during the 1–h electrolysis suggests a mechanism involving local Ge–Zn cell action. This promotes hydrogen evolution and zinc dissolution which eventually results in the deterioration of zinc deposition.

Acknowledgements

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