



The role of zinc and sulfuric acid concentrations on zinc electrowinning from industrial sulfate based electrolyte

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Abstract

The effects of varying simultaneously the zinc/acid concentrations at a fixed total sulfate, on the current efficiency, energy requirements, and deposit physical characteristics for the zinc electrowinning, using Kidd Creek zinc electrolyte, were investigated. The electrowinning experiments were conducted using a laboratory scale apparatus, at plating cycles of 24 and 30 h, a current density of 500 A m⁻² and a temperature of 38 °C. These conditions are typical of those applied at the Kidd Creek zinc tankhouse. The reagents presently used at Kidd Creek, namely strontium carbonate, Saponin, Dowfroth 250, antimony and sodium silicate, were also continuously added to the cell electrolyte at levels similar to Kidd Creek practice. Scanning electron microscopy and X-ray diffraction techniques were used to characterize the deposits with respect to morphology and preferred orientation, respectively. Cyclic voltammetry was used to study the effect of the zinc/acid concentrations on the polarization behaviour of the electrolyte. In addition, the electrical conductivity of the Kidd Creek zinc electrolyte was measured and compared with other industrial sulfate-based zinc electrolytes.

1. Introduction

One of the major goals in zinc electrowinning is minimizing the energy requirements. The two most important factors which determine the energy requirement are the cathodic current efficiency and cell voltage. A number of variables are known to affect these two factors including, zinc and sulfuric acid concentrations, current density, temperature, impurities, additives and cathode as well as anode materials.

A large number of studies have been reported in the literature that discuss the effects of the various parameters on zinc electrowinning from sulfate electrolytes. Recently the majority of these studies have focused on the effects of impurities and additives on the current efficiency, energy requirements and physical properties of the deposits. Similarly, the most recent research on zinc electrowinning using Kidd Creek electrolyte has concentrated on the individual and combined effects of additives and impurities as indicated in the various articles resulting from the collaborative research program between Kidd Creek and CANMET [1–4]. However, much less has been reported on the influence of zinc and acid concentrations.

The objective of the present work was to study the effects of varying simultaneously the zinc and acid

concentrations at fixed total sulfate on the current efficiency, energy requirements, deposit characteristics and polarization behaviour of a Kidd Creek zinc electrolyte. In addition, the electrical conductivity of the electrolyte as a function of H₂SO₄ and temperature was measured and compared to other sulfate-based zinc industrial electrolytes.

2. Experimental aspects

2.1. Electrolysis apparatus

Four electrolysis cells, with water jackets, were constructed from 1/4 inch thick Lexan materials and had approximate (17.5 cm × 9.5 cm × 12.5 cm) inside dimensions. Two lead (Pb–0.7% Ag) anodes and a central aluminium cathode (supplied by Kidd Creek) were fitted into the sides of the cells to give a cathode–anode spacing of 2.5 cm. The edges of the cathode were covered first with a thick coat of a Microstop lacquer and then with plastic strips to expose a (4.5 cm × 8.5 cm) plating area. The cells had approximately 1600 ml of electrolyte.

2.2. Electrolyte composition

The cell electrolytes were prepared from spent and neutral solutions received from Kidd Creek. For experiments where the required level of zinc or acid in the cell electrolyte could not be achieved by mixing the spent and the neutral alone, deionized water and reagent grade sulfuric acid were added. It should be noted that the added sulfuric acid was of high purity. Only relatively small amounts of acid (1–5 wt %) were added which should not introduce any significant impurities to the system. The chemical analysis of the neutral and spent electrolytes is presented in Table 1.

The various reagents and their addition levels that were used in the present work are listed in Table 2. The additives were fixed in both the starting cell electrolyte and in the fresh neutral solution feed. It should be noted that Saponin and Dowfroth 250 were added at about double the current practice addition levels at Kidd Creek due to the excessive acid mist generated in the laboratory. Also, to reduce foam escape from the top of the cell with the overflow spent electrolyte, a weir made of Lexan materials was placed near the overflow outlet of each cell.

Table 1. Chemical analysis of neutral and spent solutions received from Kidd Creek and used in this work

Anolyte	Neutral	Spent
H ₂ SO ₄ (g l ⁻¹)	–	189.2
Zinc (g l ⁻¹)	167.5	51.4
Mn (g l ⁻¹)	5.49	5.22
Mg (g l ⁻¹)	–	5.13
Na (g l ⁻¹)	–	2.54
Fe (mg l ⁻¹)	7.0	5.9
Pb (mg l ⁻¹)	–	0.4
Cl (mg l ⁻¹)	–	58.0
F (mg l ⁻¹)	–	7.0
As (mg l ⁻¹)	<0.01	<0.01
Bi (mg l ⁻¹)	<0.01	<0.01
Sb (mg l ⁻¹)	<0.01	0.012
Cd (mg l ⁻¹)	<0.1	–
Co (mg l ⁻¹)	<0.1	–
Cu (mg l ⁻¹)	<0.1	–
Se (mg l ⁻¹)	<0.01	<0.01
Sn (mg l ⁻¹)	<0.01	<0.01

Table 2. Starting zinc and acid concentrations

Zinc concentration/g l ⁻¹	27	38	42	46	50	62	73	85	96	108
Acid concentration/g l ⁻¹	228	209	202	196	190	171	152	133	112	95

Table 3. The reagents and their addition levels used in the electrowinning experiments

Reagent	Dowfroth 250	Antimony	Sodium silicate	Saponin	Strontium carbonate
Value	8 ppm	10 ppb	16 ppm	8 ppm	70 ppm

2.3. Experimental procedure and program

The four cells were connected in series to a constant d.c. power supply (Xantrex, model XKW 40-25), which can supply up to 40 V and 25 A. The temperature of the cells electrolyte was maintained at the test temperature (38 °C) by circulating heated water through the water jackets. A Haake 9 water heater was employed to heat, control and circulate the water around the cells in series. The feed electrolytes (fresh neutral solution with the required additives) were pumped into the cells at a certain flowrate using a peristaltic pump (Cole–Palmer Masterflex). The flowrate of the fresh neutral solution was set at a selected value to maintain a constant zinc concentration during the entire plating cycle. In experiments where the required flowrates were too small for the pump, an electronic power switching time controller was used to control the pump such that the desired flowrate was obtained. The cell electrolyte was internally circulated to provide agitation. At the end of the experiments, the electrolytes were analysed for zinc by atomic absorption spectrophotometry.

In this experimental program, the test work was designed to study the effects of zinc/acid concentration, for plating cycles of 24 and 30 h, current density of 500 A cm⁻² and temperature of 38 °C on the current efficiency, energy consumption, and deposit characteristics. The zinc and sulfuric acid concentrations in the cell were varied in the ranges of 27–107 g l⁻¹ and 95–228 g l⁻¹, respectively, in various combinations. Table 3 presents the starting zinc and acid concentrations. During the electrowinning experiments, the temperature and cell voltage were monitored and recorded with time using computer data acquisition system.

After electrolysis, the cathodes were immediately pulled out from the cells, rinsed with tap water and deionized water. The deposits were then stripped, dried and weighed. The weight of the deposits was used to calculate the current efficiency using Faraday's law. Sections of the deposits were examined by X-ray diffraction (XRD) to determine the preferred orientation and by scanning electron microscopy (SEM) to determine the surface morphology and microstructure.

The effect of varying the zinc/acid concentration on the polarization behaviour of zinc deposition was studied using cyclic voltammetry (CV). The CV experiments were carried out at 38 °C, employing a Solartron

1286 electrochemical interface. An aluminium cathode (0.25 cm^2), a platinum foil counter electrode and a saturated calomel electrode (SCE) reference electrode were used. The cathode was prepared by polishing down to $5 \mu\text{m}$ alumina before each experiment. The potential was cycled between -0.7 and -1.2 V with respect to SCE at a scan rate of 5 mV s^{-1} . Before each experiment, the cathode was immersed in the electrolyte until a stable rest potential was measured.

The electrical conductivity of the electrowinning electrolytes as a function of sulfuric acid concentration was measured with a conductivity meter (Copenhagen Radiometer, type CDM 2d) in conjunction with a high conductivity cell (type CDC 104) at 22, 30, 38 and $45 \text{ }^\circ\text{C}$. The cell was calibrated with a standard KCl solution.

3. Results and discussion

3.1. Zinc and acid concentrations

The change in current efficiency as a function of simultaneously varying the zinc and acid concentration in the cell electrolyte at plating cycles of 24 and 30 h are shown in Figure 1. It can be seen that for both cases, increasing the zinc concentration (decreasing acid concentrations) increased the current efficiency in a non linear fashion and that the highest rate of increase occurred when the zinc concentration was increased from 42 to 50 g l^{-1} . Within the entire range of zinc concentration tested, increasing the plating cycle from 24 to 30 h had little influence on the current efficiency and it ranged from 83% at 42 g l^{-1} to $\sim 95\%$ at 107 g l^{-1} zinc. The observation that the current efficiency decreases as the acid concentration increases is mainly due to the increase in the zinc deposition reaction rate as the number of zinc ions in the electrolyte rises. Also, since the number of H^+ ions in solution decreases, the rate of hydrogen evolution reaction is reduced. Both of these factors improve the current efficiency. These results are in good agreement with

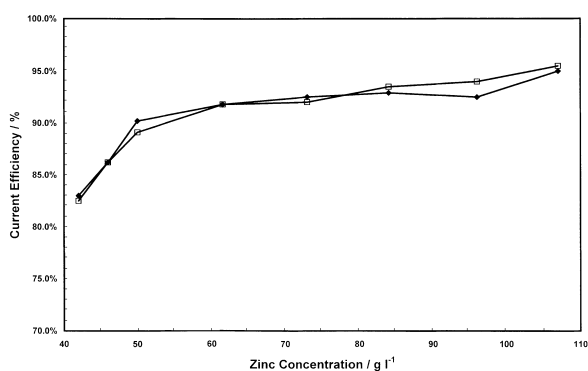


Fig. 1. Effects of zinc concentration in the electrolyte on current efficiency for 24 and 30 h plating cycles. Key: (◆) 24 h and (□) 30 h.

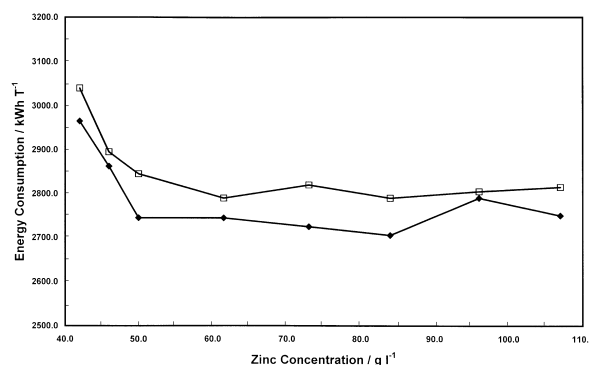


Fig. 2. Effects of zinc concentration in the electrolyte on energy consumption for 24 and 30 h plating cycles. Key: (◆) 24 h and (□) 30 h.

those reported by other investigators [6, 7]. Kidd Creek is presently stripping the zinc cathodes every 30 h.

The effect of zinc/acid concentration on the energy consumption for 24 and 30 h are shown in Figure 2. It can be seen that, for both plating cycles, the energy consumption initially decreased sharply as the zinc concentration increased from 42 to 50 g l^{-1} as a direct result of the sharp increase observed in the current efficiency (Figure 1). Above 50 g l^{-1} zinc, the energy consumption started to level off somewhat as the relatively small current efficiency gains were reduced and offset by the increasing cell voltage (Figure 3).

The cell voltage was continuously measured for the duration of the experiment using a computer data acquisition system. Manual measurements were also performed during the day to double check the data acquired by the computer and in case of malfunction of the computer. Figure 3 presents the change of cell voltage with plating time for the case of 30 h tests and it shows that the cell voltage drops as the zinc concentration decreases. This behaviour can be attributed mainly to the rise in the electrolyte electrical conductivity resulting from the higher acid levels.

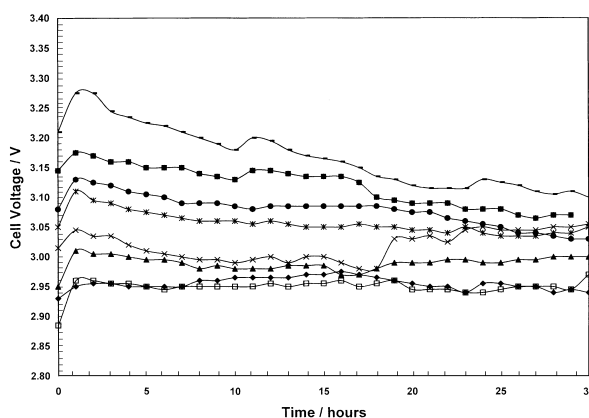


Fig. 3. Change of cell voltage as a function of time at various zinc concentrations. Concentration: (◆) 42.0, (□) 46.0, (▲) 50.0, (×) 61.5, (*) 73.0, (●) 84.5, (■) 96.0 and (■) 107.5 g l^{-1} Zn.

Within the experimental conditions considered in the present work, varying the zinc/acid concentration in the electrolytes, at both plating cycles, had significant effects on the surface morphology and the preferred orientation of the deposits. At any given zinc/acid concentrations combination, the morphology and preferred orientation of the deposits produced at 24 and 30 h were the similar. Figure 4 shows a series of SEM micrographs illustrating the effect of zinc/acid concentration on the morphology for 24 h deposits. At the low zinc concentration of 42 g l^{-1} the deposits consisted of nodules comprised of zinc platelets. These nodules were severely corroded due to zinc dissolution and the zinc grains were poorly defined (Figure 4(a)). Furthermore, a certain amount of zinc sulfate precipitates (as confirmed by EDX analysis) in the form of needle-like morphology were also observed on the deposit. The zinc platelets were aligned parallel to the aluminum cathode thus giving a predominantly (0 0 2) basal preferred orientation. The preferred orientation of the deposits produced at various zinc/acid concentrations is shown in Table 4.

The deposits plated at zinc concentrations between 46 g l^{-1} and 84.5 g l^{-1} showed little or no zinc dissolution and the hexagonal zinc platelets were much sharper, Figure 4(b). The preferred orientation changes from the basal to an intermediate preferred (1 0 2) (1 0 3) (1 1 0) (2 0 1) orientations. These types of orientations are commonly observed for industrially produced zinc deposits [2, 3].

The deposits produced in the highest zinc concentration range ($96\text{--}107.5 \text{ g l}^{-1}$) did not show the nodules observed for the other deposits, but still consisted of relatively fine zinc crystals aligned almost perpendicular to the cathode (Figure 4(c)). The structure of the deposits had a (1 0 1) (1 0 2) (1 0 3) preferred orientation. This type of morphology was observed previously by other investigators for zinc electrowon from Kidd Creek electrolytes [2].

3.2. Cyclic voltammetry

Figure 5 shows a typical voltammogram obtained for the initial electrolyte containing 50 g l^{-1} zinc. For details on the description of the various portion of the cyclic voltammetry curve refer to [2]. The nucleation overpotential (NOP) which is the distance A–B on the

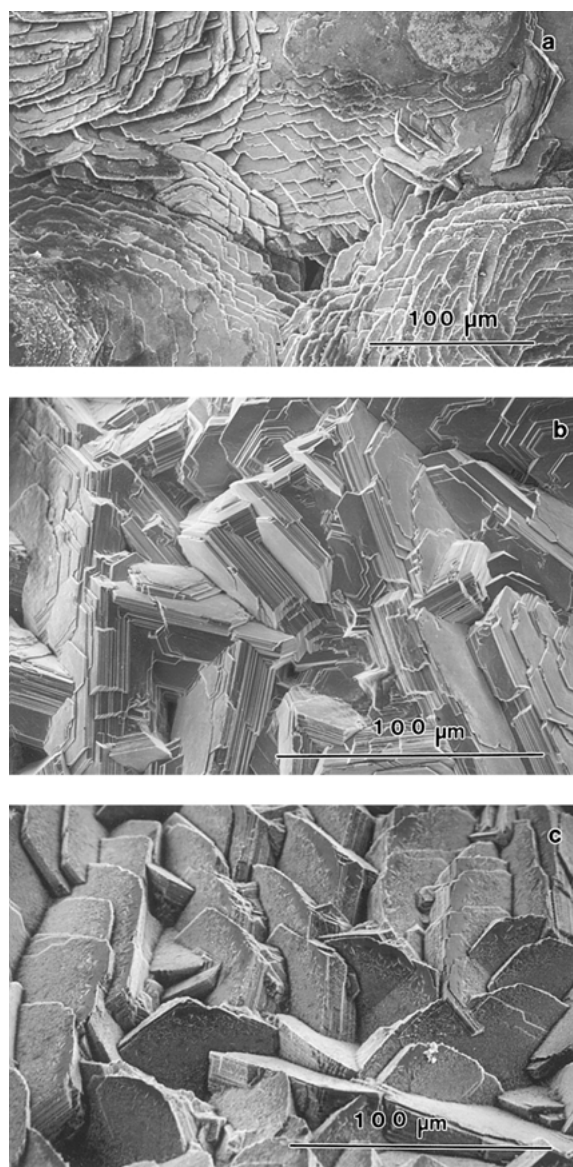


Fig. 4. SEM micrographs of zinc deposits electroplated at 24 h plating cycles at (a) 42 g l^{-1} zinc, (b) 73 g l^{-1} zinc and (c) 107 g l^{-1} zinc.

voltammogram in mV was measured and the values obtained for the starting electrolytes for the various zinc/acid concentration combinations in the electrolyte. The results represent the average of two experiments and indicate that the NOP ranged between 70 and 84 mV and did not change significantly with varying the

Table 4. Preferred orientation of zinc deposits produced at various starting zinc concentrations at 24 and 30 h

Zinc concentration/ g l^{-1}	Preferred orientation	
	24 h	30 h
42	(0 0 2) (1 0 3)	(0 0 2) (1 1 0) (2 0 1)
46	(0 0 2) (1 0 3) (1 1 0)	(1 1 0) (1 0 3) (0 0 4)
50	(1 0 2) (1 0 3) (1 1 0) (2 0 1) (1 1 4)	(1 1 0) (1 0 1) (1 0 3) (2 0 2)
61	(1 0 1) (1 0 2) (1 0 3) (1 1 2)	(1 1 0) (1 0 3) (1 1 2)
73	(0 0 2) (1 1 0) (2 0 1)	(1 0 2) (1 0 3) (1 1 4)
84	(1 0 2) (1 0 3) (1 1 4) (1 1 2)	(1 0 2) (1 0 1) (1 0 3)
96	(1 0 1) (1 0 2) (1 0 3) (1 1 2)	(1 0 1) (1 0 2) (1 1 2)
107	(1 0 2) (1 0 3) (1 1 4) (1 1 4)	(1 0 1) (1 0 2) (1 1 4)

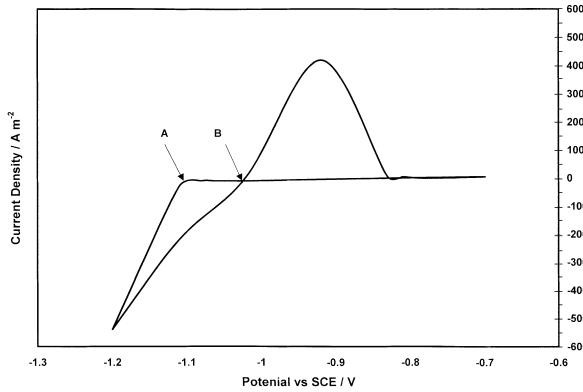


Fig. 5. Typical cyclic voltammogram for the electrolyte containing 50 g l^{-1} zinc.

zinc/acid concentration in the electrolyte. In comparison with the literature data, these values are lower by $> 50 \text{ mV}$ than those measured previously by CANMET on Kidd Creek electrolytes [2]. This variation could be due to a number of factors. The most important one may be the electrolyte composition since different electrolyte chemistry and additives were used in their study. Another factor is the cathode surface finish. In this study the final polish at $5 \mu\text{m}$ alumina was used while the cathode surface finish in the CANMET study was not specified but probably was much coarser.

3.3. Electrical conductivity

The electrical conductivity of the solution as a function of the acid concentration was measured at different temperatures and the results are shown in Figure 6. As can be seen, the electrical conductivity increases linearly as the acid concentration increased reaching a high value of 0.420 S cm^{-1} at 190 g l^{-1} acid at 38°C . As expected, the conductivity increases as the temperature of the electrolyte increases from 22 to 45°C . The values fall well within the range of the conductivity of industrial zinc sulfate electrolytes [7].

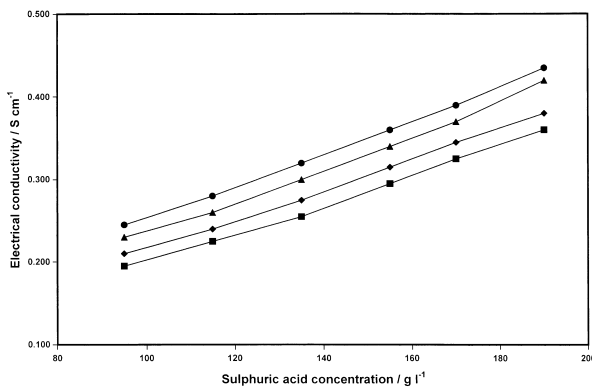


Fig. 6. Change of electrolyte electrical conductivity as a function of sulphuric acid concentration for total sulfate concentration at different temperatures. Key: (■) 22°C , (◆) 30°C , (▲) 38°C and (●) 45°C .

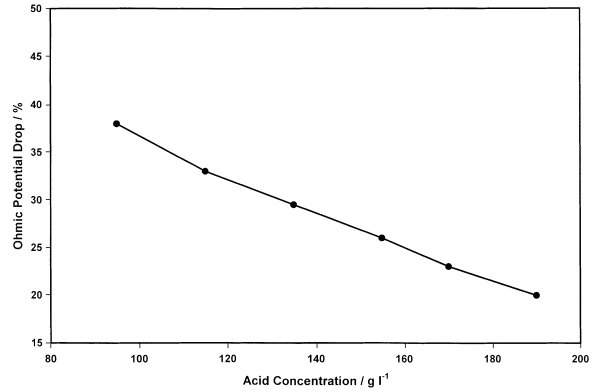


Fig. 7. Estimated percentage of ohmic drop relative to total cell voltage as a function of sulfuric acid concentration for total sulfate concentration.

The ohmic potential drop in the electrolyte is a major energy consumer and it is second only to the anode overpotential in energy consumption in zinc electro-winning [8]. In this study the ohmic potential drop was measured against SCE. Figure 7 illustrates the effect of acid concentration on the percentage of the cell voltage due to ohmic potential drop. As can be seen, the percentage of the cell voltage due to ohmic drop across the electrolyte between the electrodes decreases almost linearly with the acid concentration. The percentage of ohmic drop at 95 g l^{-1} acid is about 38% of the total voltage compared to only 22% of the total voltage at 195 g l^{-1} acid.

4. Conclusions

The following conclusions may be drawn:

- (i) For both 24 and 30 h plating cycles, the current efficiency increases with increasing zinc concentration (decreasing acid concentration) in a nonlinear fashion ranging from a low range of about 82–83% at 42 g l^{-1} zinc (202 g l^{-1} acid) to a high value of about 95% at 107.5 g l^{-1} zinc (95 g l^{-1} acid). A sharp increase in the current efficiency occurred when the zinc concentration was increased from 42 to 50 g l^{-1} , while the effect was much less dramatic for zinc concentrations higher than 50 g l^{-1} .
- (ii) The energy consumption decreases sharply from 2975–3050 to 2750–2850 kWh t^{-1} as the zinc concentration increased from 42 to 50 g l^{-1} . Above 50 g l^{-1} zinc, the energy consumption starts to level off somewhat at about 2750–2850 kWh t^{-1} as the relatively small current efficiency gains were reduced and offset by the increasing cell voltage.
- (iii) At both 24 and 30 h plating cycles, varying the zinc/acid concentration in the electrolytes had significant effects on the surface morphology and the preferred orientation of the deposits. At the low zinc concentration of 42 g l^{-1} the deposits consisted of nodules comprised of zinc platelets. These

nodules were severely corroded due to zinc dissolution and the zinc grains were poorly defined. The zinc platelets were aligned parallel to the aluminium cathode thus giving a predominately (0 0 2) basal preferred orientation.

- (iv) The deposits plated at zinc concentrations between 46 g l^{-1} and 84.5 g l^{-1} showed little or no zinc dissolution and the hexagonal zinc platelets were much sharper. The preferred orientation changes from the basal to a random preferred (1 0 2) (1 0 3) (1 1 0) (2 0 1) orientations. These types of orientations are commonly observed for industrially produced zinc deposits.
- (v) The deposits produced in the highest zinc concentration range ($96\text{--}107.5 \text{ g l}^{-1}$) did not show the nodules observed for the other deposits, but still consisted of relatively fine zinc crystals aligned almost perpendicular to the cathode. The structure of the deposits had a (1 0 1) (1 0 2) (1 0 3) preferred orientation.
- (vi) The nucleation overpotential (NOP) measured for the starting electrolytes for the various zinc concentrations in the electrolyte indicate that the NOP ranged between 70 and 84 mV and did not change significantly with varying the zinc/acid concentration in the electrolyte.
- (vii) The electrical conductivity increases linearly as the acid concentration increased reaching a high value of 0.420 S cm^{-1} at 190 g l^{-1} acid at 38°C . As expected, the conductivity increases as the temperature of the electrolyte increases from 22 to 45°C . It should be noted that the effect of temperature is more pronounced at the high acid concentrations. The values fall well within the range of the conductivity of industrial zinc sulfate electrolytes.

- (viii) The percentage of the cell voltage due to ohmic drop across the electrolyte between the electrodes decreases almost linearly with the acid concentration. The percentage of ohmic drop at 95 g l^{-1} acid is about 38% of the total voltage compared to only 22% of the total voltage at 195 g l^{-1} acid.

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