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A modified Hull cell and its application to the electrodeposition of zinc

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Abstract

An analytical electrochemical cell based on the Hull cell is described. The cell was tailored specifically for the analysis of electrowinning or electroplating. Current density distributions were generated by asymmetric insertion of an insulating baffle between parallel electrodes. The position and length of the baffle were easily altered, giving 12 possible distributions for a single total current. The cathode consisted of 10 electrically isolated 1 cm^2, aluminium segments. By logging the potential drop across 1 Ω resistors in each of the 10 isolated parallel branches, quantitative determination of current densities across the cathode was made possible. The small segments facilitated microscopic analysis of deposit morphologies. A technique for the determination of current efficiencies on each segment is described and demonstrated. The technique obviates the necessity to determine deposited masses directly. Development of the technique for industrial application is detailed. The system is demonstrated by evaluating known effects of variables in zinc electrowinning. The variables examined were temperature, deposition time, acid concentration and antimony contamination.

1. Introduction

The Hull cell is an analytical electrochemical cell designed with trapezoidal geometry to incorporate a range of current densities into a single experiment [1]. It was designed to examine electroplating rather than mass production processes. For such applications it is an imperfect tool with the following shortcomings. A primary current density distribution is assumed. The single plate cathode (10 cm × 6 cm) does not permit easy microscopic analysis of deposited metal at specific current densities. Electrolytes must be stagnant. It is not easy to obtain the dependence of current efficiency on current density. To obtain current efficiency it is necessary to measure the deposited mass and, unless the cathode is cut up, only the overall current efficiency is obtained.

Research studies in zinc electrowinning often employ pilot or full-scale electrowinning cells [2, 3]. Obtaining one efficiency measurement at a single current density for a given set of conditions can be a lengthy procedure. Deposition time must be sufficient to obtain a discernable mass when compared to electrode mass, and the mass must be recorded. A second problem is that of accurately isolating the effect of any single factor, particularly impurity metal ions in the electrolyte. The difficulty in obtaining absolutely pure solutions [4], the extremely low concentrations of certain impurities (ppb) which reduce current efficiency on the order of 10% [5], and the unknown synergistic effects between impurities [6, 7] cause inconsistencies in results reported throughout the literature.

Due to the problems outlined above, experimental work with the Hull cell is often empirical. For a given set of operating conditions, one variable is altered and tests are run. The corresponding changes in current efficiency are reported. It is quite possible that a different study examining the effect of the same variable will return a similar trend but different values, the reason for the discrepancy being differences in the set of operating conditions. When simulating industrial conditions an example of such a difference is the use of electrolytes obtained from different ores.

The objectives of this research were to develop an analytical electrochemical system that is an improvement on the Hull cell and to test the system by application to zinc electrowinning. Emphasis was placed on obtaining the quantitative variation of current efficiency with current density for typical variations in conditions encountered in practice. To enable the determination of current efficiency at separate current densities in a single run, a technique which obviated the need to record deposited masses directly was developed. Zinc electrowinning is an old and established process. There are several results from experiments examining the effects on efficiency of core process variables [8, 9] and impurity effects [10–12], however, in none of these studies were the results obtained using the tools and techniques developed in the present study.

2. Experimental system

The three main advantages sought from the cell (over the regular Hull cell) were a variable current density range, direct quantitative determination of current density at ten points across the cathode and easily analysed deposits.

The proposed technique to permit variation of range was asymmetric insertion of an insulating baffle close to the cathode in a similar manner to the open slot cell [13]. Unlike the slot cell, the design was to allow the position and length of the baffle to be easily altered, each configuration producing a different degree of non-uniformity. For the cell constructed, there were three positions and four lengths, which allowed a total of twelve possible distributions for a single total current. Initial investigations into the plausibility of generating a skewed current density distribution by use of a baffle were carried out on software (Cell) developed (by Professor Uziel Landau at Case Western University) specifically for the simulation of electrochemical cells. Figure 1 shows a current density distribution generated for the geometry proposed. It exhibits clearly that use of a baffle produces a distribution of the desired form.

By segmenting the cathode into ten electrically isolated 1 cm^2 segments and logging the voltage drop across 1 Ω resistors behind each segment, a direct measurement of current density at ten points across the cathode is possible without the need to assume a primary distribution. The total current can be selected rather than having to be 1, 2 or 3 A in order to match a standard test panel, which is the case for the conventional Hull cell. The small segments make ideal samples for SEM and X-ray analysis.

The cell was designed to allow continual flow through of electrolyte. The conventional Hull cell only allows testing under stagnant solutions. A commercial zinc electrowinning cell has continual flow through of electrolyte and providing the opportunity to flow electrolyte through the cell allows for simulation of the effects of this flow. Figures 2, 3 and 4 show a photograph of the cell, a cross sectional schematic of the cell and a full system schematic respectively. The body of the cell was constructed from Plexi-glass (poly-methylmethacrylate polymer); a durable, corrosion resistant polymer. The cathode segments were aluminium and the anode was a DSA mesh with a copper current feeder across the top. The anode was switched to a zinc plated aluminium plate when the polarity of the cell was reversed to avoid zinc plating onto the DSA. The data acquisition system converted analog voltages measured across eight of the ten resistors into digital signals and displayed them directly. The software used was a commercial package produced by Strawberry Tree [14].

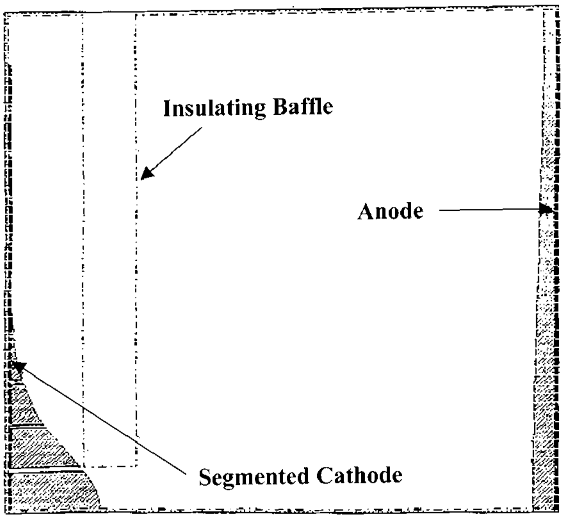

Fig. 1. Scanned image of early ‘Cell’ plot. Illustrates how baffle placement generates current density distribution.

3. Previous investigations

There are many studies in the literature devoted to modifying a Hull cell. One group particularly active in this area is that of Professor D. Landolt at the Ecole Polytechnique Féderal de Lausanne. Papers published by this group and others are reviewed in order to highlight where the present work fits in to the development of the field as a whole.

Madore et al. [15] describe design considerations for a cylindrical Hull cell with forced convection. The cell is a rotating cylinder electrode with the counter electrode placed near one end. The hybrid cell has the benefits of both the well-characterized mass transfer conditions of the rotating cylinder electrode and the asymmetric current density distribution of the Hull cell. The paper goes on to discuss design optimization using numerical simulation techniques. As in the present study, the proposed design offers the potential to examine both current density variation and flow effects simultaneously, the hydrodynamic control being undoubtedly superior. However the geometry is fixed, with no option to vary the current density distribution generated at a given

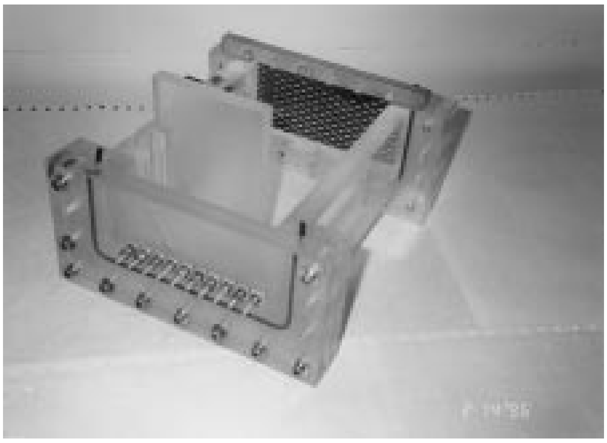

Fig. 2. Photograph of the modified Hull cell.

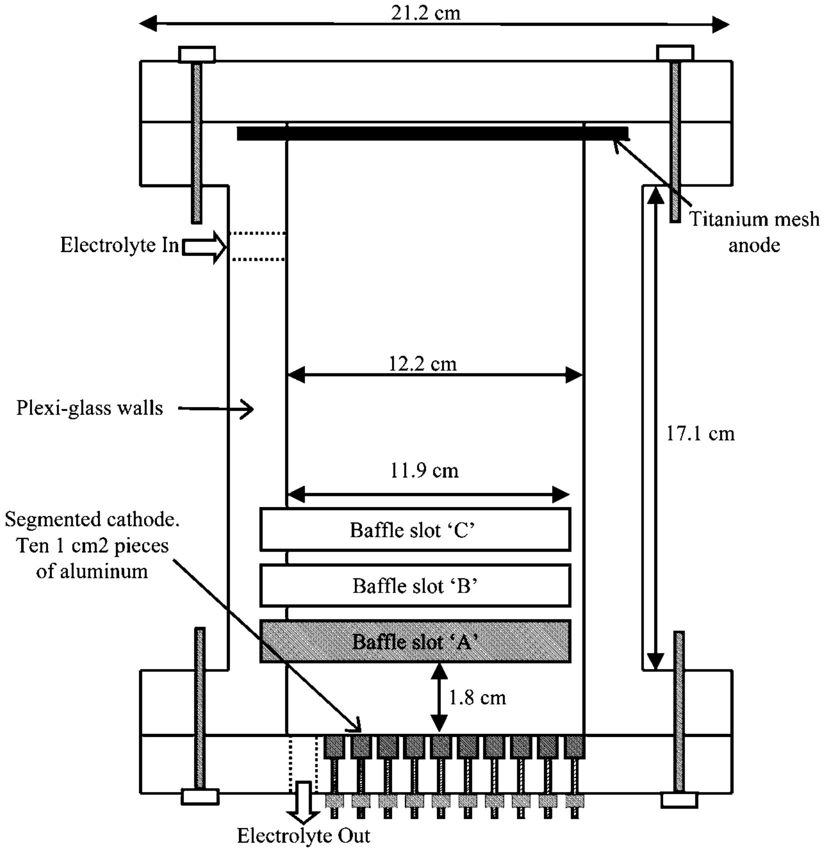

Fig. 3. Cross sectional schematic of modified Hull cell.

total current. The cathode also differs in that it is not segmented.

The same group used boundary element and finite element techniques to simulate the secondary current density distribution in a conventional Hull cell and verified the results experimentally by measuring the thickness of copper deposits under controlled deposition conditions [16]. Results were excellent, however, again the cathode was not segmented and current densities were not directly experimentally determined from charge passing at defined regions along the cathode.

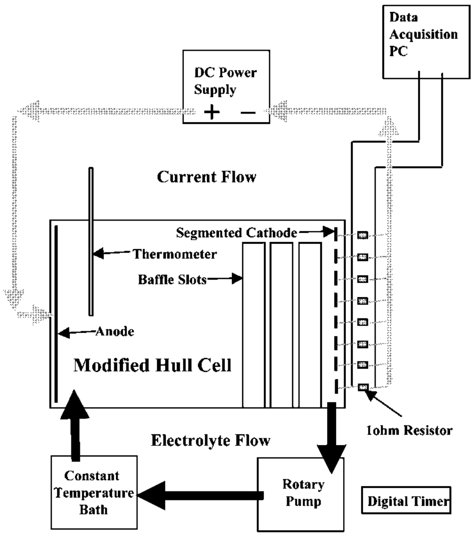

Fig. 4. Schematic of full experimental system.

A third paper by Degrez et al. [17] describes a modified Hull cell with forced flow for the simulation of industrial plating conditions and its use to examine zinc and copper electrowinning. The cell successfully facilitated the inclusion of hydrodynamic effects but only a single current density distribution was possible at a given total current and again, the cathode was not segmented. Variation in current efficiency with current density was not determined directly.

In summary, there have been several papers describing studies using and modifications to the original Hull cell. The added features of the system described here are the use of a segmented cathode and a technique to determine the current efficiency of a plating process on each segment, which obviates the necessity to determine either the deposit mass or thickness. The system enables a direct quantification of the variation in current efficiency with current density for a given plating process without the need to assume any type of theoretical distribution. Its value lies in rapid on site diagnosis of industrial electrowinning and electroplating. The aforementioned technique is described in the following Section.

4. Development

The proposed technique to measure current efficiency constituted the most novel part of the study and a description follows. The total charge passed during zinc deposition is logged (using the 1 Ω resistors behind each cathode segment). The polarity of the cell is reversed and the total charge passed to strip the deposited zinc from each segment is logged in an identical manner. The dissolution takes place at constant potential, thus when all zinc is removed from a cathode segment the current density falls rapidly, settling close to zero. During deposition, the total charge passed accounts for both zinc deposition and the side reaction of hydrogen generation. During the dissolution (up to the drop in current density towards zero) the total charge passed accounts for zinc dissolution only. There is no competing side reaction at potentials employed during dissolution. Thus the charge passed for dissolution, as a percentage of the charge passed for deposition on a single cathode segment, yields the current efficiency of that segment.

Figure 5 shows the current density history for a typical deposition/dissolution cycle on a single cathode segment using a 30 min deposition time. The Figure also shows how the charge passed during deposition and dissolution was calculated. The charge is the area under the curve and is obtained by application of a simple trapezoidal algorithm. Calculation of the current density for each segment is trivial, and hence, in a single run the evaluation of current efficiency at several different current densities is made possible.

The technique was tested using neutral, laboratory synthesized zinc sulfate solutions containing 116 g L^{-1} zinc. 1 and 2 h depositions were carried out and the efficiency was measured by both mass difference and charge comparison techniques simultaneously. Figure 6 shows the results. A high degree of agreement between the two techniques was observed. The next stage was application of the technique to industrial electrolytes containing 100–150 g L^{-1} acid and reduction of deposition time (and hence total test time). Several problems were encountered in this phase of development. Descriptions of each problem and the solutions to these problems follow.

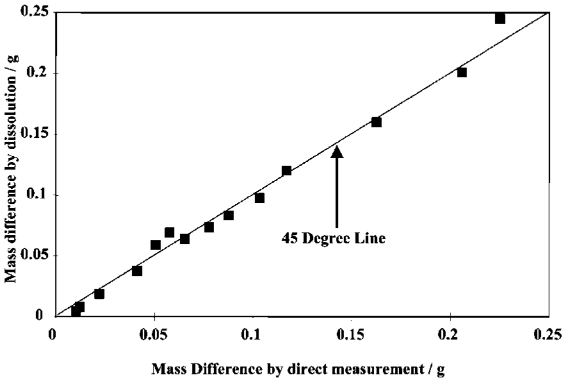

Fig. 6. Results from measuring current efficiencies by mass difference and electrodissolution techniques simultaneously.

A significant problem was the chemical attack of deposited zinc by acidic electrolytes during electrodissolution, shown schematically in Figure 7. For the efficiency measurement technique to be accurate, it is necessary for all electrodeposited zinc to be stripped electrochemically according to Reaction 1. However, for acidic electrolytes, Reaction 2 was occurring simultaneously. Hydrogen ions in the electrolyte dissolve the zinc in a chemical redox reaction with no net charge transfer. This results in the passage of an artificially low quantity of charge to remove the deposited zinc, which in turn manifests itself as an artificially low current efficiency. The problem was overcome by switching to neutral synthetic electrolyte prior to dissolution.

$$Zn \rightarrow Zn^{2+} + 2\,e^{-} \qquad (1)$$

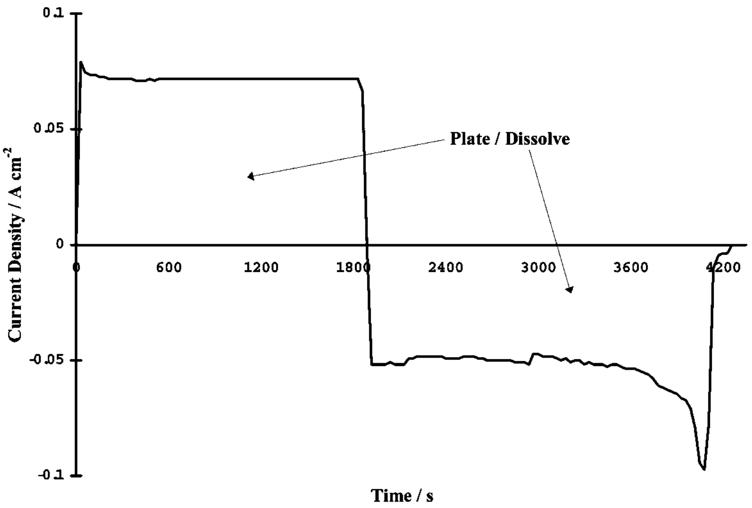

Fig. 5. Cycle schematic showing how the area under the current against time plot is integrated by the trapezoidal approximation.

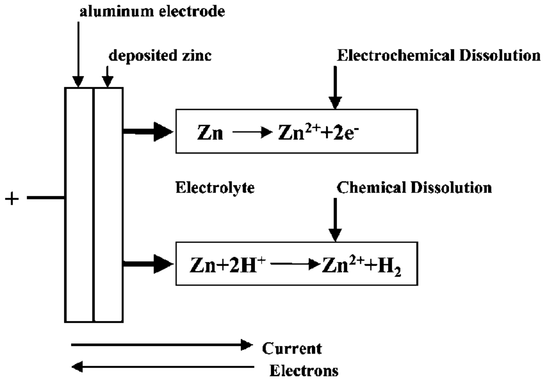

Fig. 7. Schematic illustrating chemical dissolution of deposited zinc.

$$Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2 \tag{2}$$

In many industrial zinc sulfate electrolytes manganese ions (Mn^{2+}) are inherent. The concentration of manganese ions present in the industrial electrolyte employed was 20 g L^{-1}. The manganese had no noticeable effects during deposition, zinc plating out as expected. However, during the dissolution step, a yellow film was observed across the electrode surface. The film was identified as manganese compound, presumably manganese dioxide, forming by Reaction 3, and as deposited zinc dissolved into the electrolyte, manganese oxide grew across the electrode surface.

$$2\,H_2O + Mn^{2+} \rightarrow 4\,H^+ + MnO_2 + 2\,e^- \tag{3}$$

This phenomenon drastically reduced the flow of current and effectively stopped the experiment. Figure 8 is an electron micrograph of an electrode taken after such a run. Residual zinc was still evident on the surface when current had ceased to flow. The solution to this problem was to switch to neutral synthetic electrolyte in between deposition and dissolution. If the plating electrolyte was neutral, a second solution to the problem was to reduce the dissolution current densities. It was found that a window of potential existed corresponding to current densities between 0 and ~60 A m^{-2} wherein zinc dissolved but no film formation was observed. Zinc dissolution was the favourable and only reaction in this potential range.

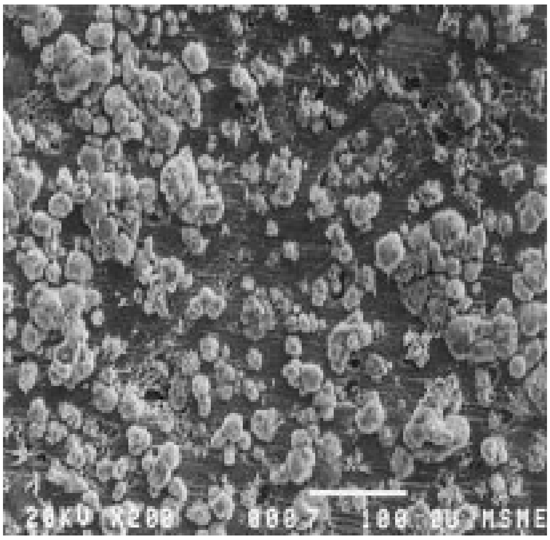

Fig. 8. SEM microgrograph showing undissolved residual zinc due to the formation of a yellow oxide film across the electrode substrate from an electrolyte containing manganese.

An advantage sought from the efficiency measurement technique was shorter test times. Initial experiments with deposition times of 3 and 5 min gave unsatisfactory reproducibility. The problem lay in the determination of the dissolution end point. The currents on a segment do not fall completely to zero after the zinc has been stripped. Small residual currents exist due to the dissolution or anodization of aluminium and/or oxygen evolution at the electrode surface. For longer deposition times, and hence larger masses of zinc, the errors associated with correctly determining this point are negligible and reproducibility is satisfactory. For shorter times and therefore smaller masses, the errors become significant. Figure 9 shows current density histories for three successive plate/dissolve cycles on the same segment for a deposition time of 3 min with neutral, industrial electrolyte and illustrates the problem.

A solution was found at the expense of total test time. By switching to neutral synthetic electrolyte for dissolution and reducing the dissolution current densities to 50% of the corresponding deposition densities, residual currents became negligible and accurate end point determination was made possible. At these lower current densities the resolution of the data acquisition system was increased from 3 to 6 decimal places in order to maintain acceptably small errors during numerical integration.

Figure 10 exhibits the final problem to be addressed in the development of an experimental procedure. The first run in a sequence of runs gave reduced current efficiencies for all current densities. The low efficiency values observed during the first run were thought to be real values, observed due to electrochemical phenomena during the initial deposition, rather than artificially low values due to problems during dissolution. The explanation was hypothesized as one, or a combination, of the two following phenomena:

(i) The electrode surface topology (e.g., corrosion pits) required time to become fully wet and reach a steady state in terms of electrochemistry.

(ii) The oxide layer that coats the initially dry electrodes required time to be broken down by hydrogen ions in the electrolyte. During this period zinc deposition is hindered.

The second reason was deemed more influential, as it was observed experimentally, that the degree of anomaly decreased as the initial acid concentration in the electrolyte increased. A solution was found at the expense of test time. By soaking the electrode surfaces for a period of time before initiating electrolysis, the first

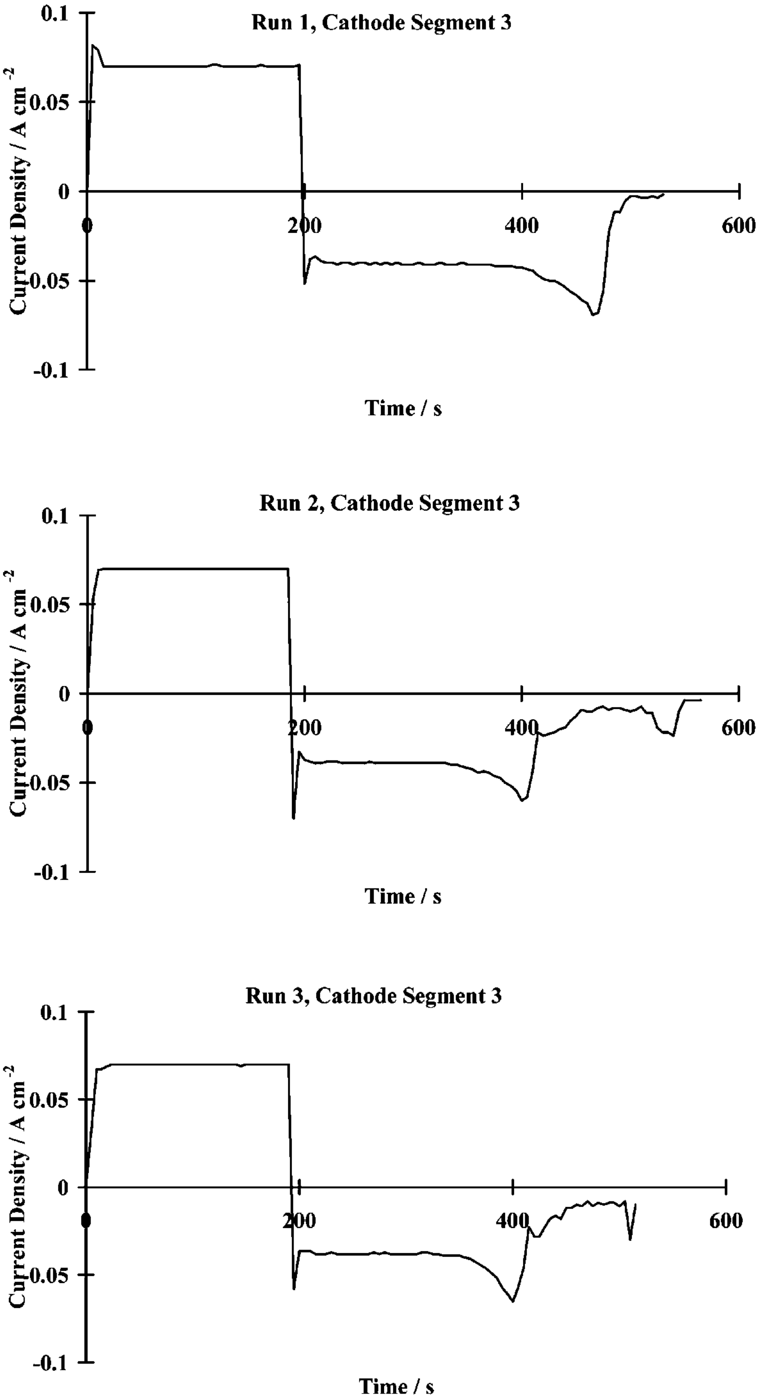

Fig. 9. 3 Consecutive plate dissolve cycles for a 3 min deposition time on cathode segment 3. Highlights dissolution end point ambiguity.

run anomalous behaviour was no longer evident. Figure 11 shows efficiency versus density plots for a sequence of 5 min depositions from an acidic, industrial electrolyte. The electrodes were presoaked for 20 min. The results exhibit excellent reproducibility with current efficiencies in the expected range. An experimental procedure allowing application of the technique to acidic, industrial electrolytes for a deposition time of 5 min had been established and is formalized hereafter.

The temperature bath is set at 40 °C. 600 ml of electrolyte is poured into the cell and circulated. The electrolyte reaches steady state temperature after 5 min and is circulated at this temperature for a further 20 min. Electrodeposition is carried out for 5 min. Electrolysis is halted and the electrolyte is tipped from the cell. The deposit is thoroughly rinsed with prewarmed, neutral, synthetic electrolyte containing 116 g L^{-1} zinc. 600 ml of that electrolyte is added. The polarity of the cell is reversed, the DSA anode is switched to preplated aluminium (preplated with zinc) and dissolution of the deposit commences. The dissolution densities are typically one half to one third of the value of the corresponding deposition densities in the range 250 to 50 A m^{-2}. When current densities through

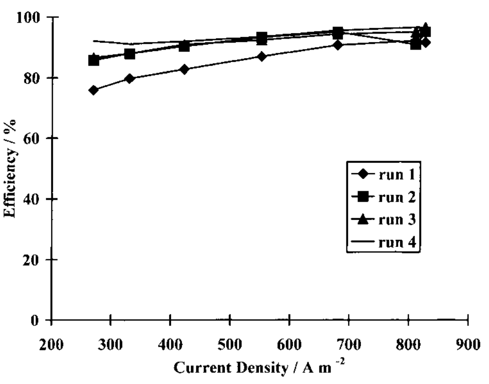

Fig. 10. Four consecutive 5 min depositions from industrial electrolyte. Deposit rinsed and electrolyte changed to neutral synthetic for dissolution. Illustrates improved reproducibility and first cycle anomaly.

all segments have exhibited a dramatic decrease towards zero the cycle is complete.

5. Results

The previous Section outlines the progression to an experimental procedure free from systematic error. Throughout the refinement of that procedure, the cell and technique were being used to generate data on the effects of changing variables in the zinc electrowinning process. Earlier results were subject to systematic errors inherent to the core procedure and are not included with one exception. The investigation of temperature effects is such a result and is shown for two reasons. First, it exhibits clearly the problems caused by chemical dissolution of deposited zinc and, secondly, because it gives a striking example of the systems capacity to discern expected trends when absolute values were distorted.

5.1. *Effect of temperature*

Figure 12 shows the results from a set of four sequences of experiments run at 27, 37, 47 and 57 °C. The lowest temperature was set at the ambient temperature of the laboratory. Higher temperatures were set by the constant temperature water bath controlled by a thermostat. The electrolyte employed was synthesized from reagent grade zinc sulfate and sulfuric acid. The concentrations were set at 78 g L^{-1} zinc and 35 g L^{-1} acid. There was no switching of electrolyte to neutral for electrodissolution. Deposition time was 30 min.

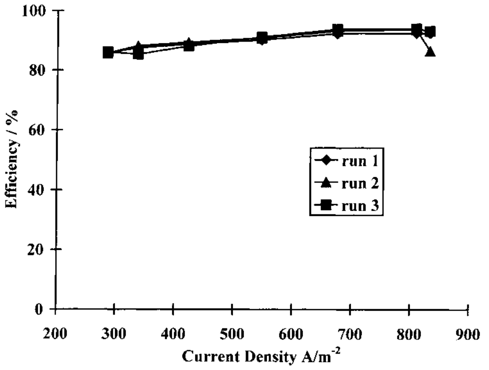

Fig. 11. Three consecutive 5 min depositions from industrial electrolyte. Electrodes soaked in acidic plating electrolyte for 20 min prior to electrolysis to remove first run anomalous behaviour.

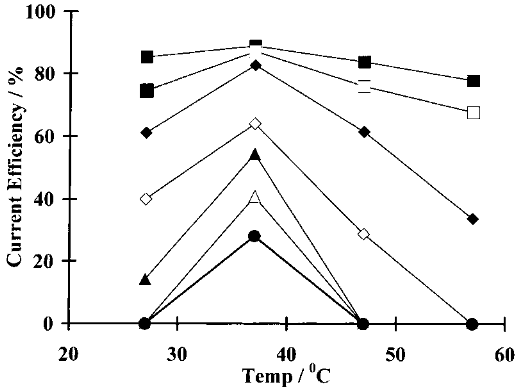

Fig. 12. Current efficiency against temperature at increasing current densities. Current density: (■) 732, (□) 563, (◆) 297, (◇) 149, (▲) 98, (△) 94 and (●) 91 A m^{-2}.

This was an encouraging early result, as it clearly defined an optimal operating temperature in the region of 40 °C across the whole range of current densities. This is reported in the literature [9]. However, the reported optimum is usually with reference to power consumption, due to increased electrolyte conductivity

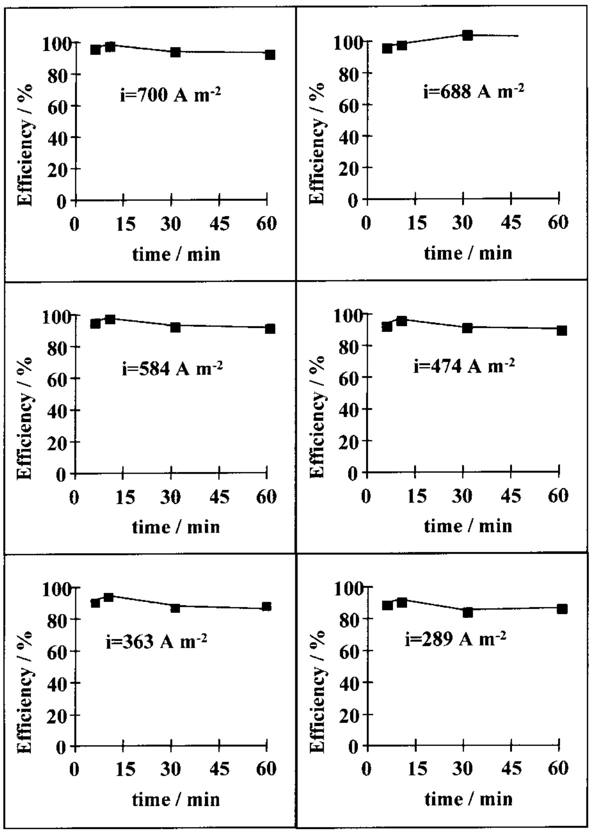

Fig. 13. Current efficiency against deposition time at increasing current densities. Electrolyte switched to neutral for dissolution.

at higher temperatures decreasing cell voltage for a given current density. Variations in CE with temperature were similar but less pronounced, and were not reported to drop off radically above 45 °C as suggested by Figure 12. The upper limit was set by the undesirable nodular and dendritic deposit morphologies observed at temperatures in excess of ~50 °C. Such morphologies were also observed in this study, and played a role in determining the form of Figure 12 discussed below.

For the current efficiency measurement technique to be accurate, it was necessary for all deposited zinc to be removed electrochemically. At higher temperatures, the deposit morphologies on higher current density segments were nodular or dendritic, and hence physically fragile. At times, the force of the flowing electrolyte would wash small parts of the deposit off the electrode. Such deposit break off consequently resulted in artificially low current efficiencies, and was the key-contributing factor to the drop in current efficiencies observed above 45 °C for the top three segments. Deposit break off was the most significant influence of electrolyte flow. Experiments examining flow through effects revealed a negligible impact on current density distribution in the current density range selected, deposition being controlled by electrode reaction kinetics and not mass transfer to the surface. For dissolution into acidic electrolytes, flow increased the detrimental effect of chemical attack, giving efficiencies reduced in the order of 5–10% when compared to results for a stagnant solution with all other conditions constant.

Figure 12 suggests that the low current densities are below the critical current density (current density below which no zinc deposition occurs) at temperatures under ~25 °C and above ~47 °C. This is possible at the lower temperature, however, at the higher temperatures, once increased deposition kinetics were sufficient for plating to have occurred, there seems little basis for the observed drop to zero at 47 °C. The explanation for this observation is the chemical attack of the deposit described in Section 3. The effect is magnified for small deposited masses, low dissolution current densities and enhanced chemical dissolution rates at elevated temperatures. In summary, the results gave an optimal temperature of the correct value and insight into limitations of the efficiency measurement technique with regard to dendrite break off. Results at low current densities were significantly distorted by chemical dissolution of the electro-deposit.

5.2. *Effect of deposition time*

Figure 13 shows the efficiencies obtained from deposition times of 5, 10, 30 and 60 min from neutral industrial electrode acidified with 50 g L^{-1} reagent grade concentrated sulfuric acid using the finalized procedure with baffle configuration '3B'. The temperature employed was 40 °C and the zinc content was 120 g L^{-1}. As expected, and previously reported, current efficiency is close to constant with time at a given current density. There is a slight decrease in efficiencies with current density, however, values are consistently in excess of 90% at current densities above ~300 A m^{-2}. This agrees with efficiencies observed in industrial electrowinning.

5.3. *Effect of initial acid concentration*

Using the finalized experimental procedure detailed in Section 3, four experiments using industrial electrolyte with initial acid concentrations of 0, 50, 100 and 150 g L^{-1} were carried out. Baffle configuration '3B' was employed. The depositions were run at successively decreasing potentials so that current densities on all the cathode segments were the same for every run. This allowed the plotting of results from all four experiments on the same axis. Figure 14 exhibits efficiency vs. acid concentration plots at six current densities obtained in this study.

The values and trend concur with those reported in the literature [8, 9] and observed in industry. There is some decrease in current efficiency with increasing acid concentration, particularly at lower current density. Efficiencies are slightly reduced at lower current densities, the trend with acid concentration remaining almost constant. At current densities close to 500 A m^{-2}, efficiencies remain in the region of 90% for acid concentrations up to the maximum examined (150 g L^{-1}).

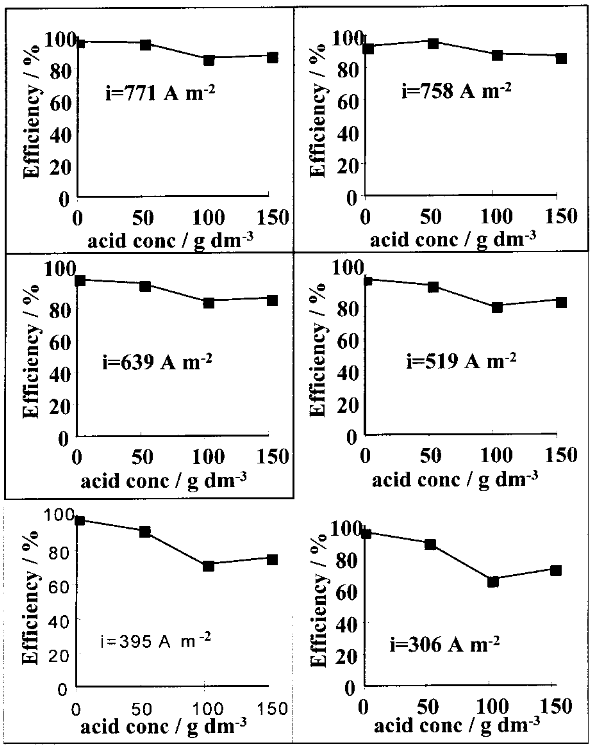

Fig. 14. Current efficiency against initial acid concentration at increasing current densities. Electrolyte switched to neutral for dissolution.

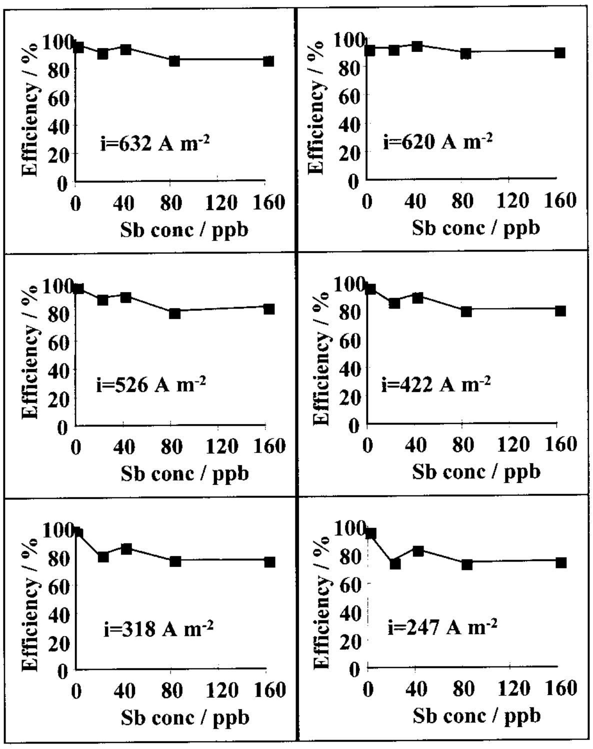

Fig. 15. Current efficiency against antimony concentration in the electrolyte (ppb) at increasing current densities. Electrolyte switched to neutral for dissolution.

5.4. *Effect of antimony*

Figure 15 shows results obtained examining the effects of the presence of trace concentrations of antimony. The electrolyte employed was the same as that used for the study of deposition time with the addition of 0, 20, 40 and 80 ppb of antimony. The baffle geometry used was '3B', which generated a range of current densities from 632 to 247 A m^{-2}. The plots show that the greatest reductions in current efficiency observed are in the region of 20% and the current efficiency is most sensitive to antimony at the lower current densities. A reduction in current efficiency of this magnitude is enormous considering the minute levels of antimony contamination and the results are a vivid example of the potential detriment trace impurities can have on the zinc electrowinning process.

6. Conclusions

An analytical electrochemical cell was designed and developed. By positioning an insulating baffle close to the cathode between parallel electrodes, the electric field was distorted in such a way as to produce a distribution of current densities across the cathode. The cell designed had three possible baffle positions and four baffle lengths which permitted a total of twelve different distributions for a single total current, as opposed to a single distribution for the Hull cell. The successful implementation of a segmented cathode permitted direct determination of current densities across the cathode as opposed to an assumed primary current density distribution in the case of the Hull cell. The segmented cathode also provided ideal deposit samples for SEM and X-ray analysis.

A technique for the determination of current efficiency was developed. By logging the charge passed in the deposition and subsequent stripping of a given mass of zinc, the direct measurement of the deposited mass was obviated. This decreased test time and enabled quantification of the variation of current efficiency with current density across the cathode. The technique was initially tested on neutral synthetic electrolytes for 1 and 2 h deposition times. An experimental procedure was developed to permit use of the technique with acidic industrial electrolytes and a deposition time of 5 min. The modified Hull cell and technique were used in tandem to diagnose the effects on current efficiency of changing variables in the zinc electrowinning process. The system successfully determined the influence of temperature, acid concentration, deposition time and antimony concentration.

Acknowledgement

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