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The coulombic efficiency of zinc electrowinning in high-purity synthetic electrolytes

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Measurements of coulombic efficiency (QE) for zinc electrodeposition were carried out under mass transfer-controlled conditions using a rotating disc electrode in synthetic acidic zinc sulphate electrolytes. At 25° C in 0.8 M $ZnSO_4$ + 1.07 M H_2SO_4 prepared from reagent grade chemicals, the QE at an aluminium cathode was 95.7–97.6%. In order to study the influence of electrolyte purity on QE several preparation and purification techniques were employed. While different sources of chemicals produced different QEs, the main source of impurities seemed to be the zinc-containing reagent rather than the sulphuric acid. Improvements in purity either had a negligible effect or lowered the QE, indicating that some impurities are beneficial to electrolyte performance. In the purest solutions prepared, an effect due to residual impurities still seemed to be present. The maximum QE obtainable through variation of the three parameters, i.e. temperature, current density and electrode rotation rate, was determined for two electrolytes of different purities; the values of QE obtained were 98.4 and 98.8%, with temperature as the dominant factor. 'Wark's Rule' (the dependence of QE on zinc/acid ratio) was obeyed approximately in the purest electrolyte prepared, over a limited range of composition.

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1. Introduction

Under plant conditions, coulombic efficiencies[†] (QE) for the zinc electrowinning process generally fall in the range 85–93% [1]. The zinc electrolyte contains many components in addition to the zinc sulphate and sulphuric acid. Major components include manganese, magnesium, sodium and potassium and these are thought to have little effect on QE. Many of the 20 or more detectable trace impurities as well as the additives used to control the process can affect QE. The upper limit for QE obtainable with plant electrolytes is unknown, since the electrodeposition conditions will usually have been defined by experience and/or limited small-scale tests. Indeed, criteria other than QE, for example, power efficiency, rate of anode corrosion and zinc metal purity, may have been used in setting plant process conditions.

Laboratory studies on zinc electrowinning are in general concerned with the influence of certain impurities on QE and zinc deposit morphology [2–6], rather than with the influence of improving electrolyte purity on the QE. Methods for measuring QE in the laboratory have generally not been at issue, except where the work was directed towards the development of plant–electrolyte purity meters [7–10]. In fact, it is often difficult to compare the results of impurity effect studies because of differences in QE measurement techniques, composition and

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[†] We use the term coulombic efficiency (QE) in preference to the term current efficiency (CE) since it properly describes the measured yield of zinc (converted to charge) expressed as a fraction of the total charge passed. The CE properly refers to an instantaneous quantity, the ratio of the partial *current* for zinc deposition to the total current. The two quantities are not the same in this work since, as we shall show, CE varies with time. While common usage in the electrowinning area is to report results as CE, authors are usually referring to QE.

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purity of the electrolytes and electrodeposition conditions.

The requirement for extreme purity of zinc electrowinning electrolytes was discussed as early as 1922 by Tainton [11]. In later work, Znamenskii and Stender [12] and Salin [13] reported that QE was a function of purity of the starting materials. QE increased from 94–95% for an electrolyte prepared from a commercial grade of zinc to 98–99% for an electrolyte made from 99.9999% zinc, doubly sublimed H_2SO_4 and triply distilled water. A reasonable inference from such studies is that the purer the electrolyte, the higher will be the QE; how closely a QE of 100% is approached in the complete absence of impurities is as yet unknown. However, Wark [14, 15] has proposed a relationship between the initial CE and the zinc/acid ratio of the electrolyte which does not allow a CE of 100%, except as a limiting case, regardless of intrinsic electrolyte purity. A theoretical basis for such a relationship was later derived by Bratt [16]. One of our objectives was to reappraise the question of the upper limit of QE in high-purity electrolytes.

In the present work the QE was determined from the weight of zinc electrodeposited onto a rotating cathode under galvanostatic conditions, as described by Biegler and Swift [17]. The control of hydrodynamic conditions afforded by the rotating disc electrode (RDE) is necessary where the QE is suspected of being influenced by trace impurities whose deposition is mass transfer-controlled. The precise determination of QE possible in the laboratory offers the opportunity to establish the conditions under which QE approaches a maximum. A statistical method was employed to optimize QE for two electrolytes of different purity and to help in the establishment of the upper limit of QE.

Various methods of electrolyte preparation and purification were investigated and the corresponding QE determined. One method involved the purification of an electrolyte prepared essentially from analytical grade reagents, while another involved direct preparation of electrolytes from reagents of a very high purity. It is of course impossible to define the purity obtained except in terms of measured concentrations and limits of detection of known deleterious impurities (usually cations) by available analytical methods. In the present study electrolytes were analysed for trace impurities using either anodic stripping voltammetry (ASV) or the inductively coupled plasma (ICP) technique.

2. Experimental details

The QE measurements were carried out under mass transfer-controlled conditions in a glass electrochemical cell especially designed to minimize contamination of the catholyte by anode products. The cell and the preparation of $\sim 2\,\text{cm}^2$ aluminium cathodes have been described previously [17]. Cathodes of the same area were also fabricated from zinc (special high grade, 99.995%), lead (99.99%), indium (99.9%) and glassy carbon (Sigradur K) with Kel-F sheaths, to fit a Tacussel type EDI electrode rotator. The surface of the electrode was lightly ground with P1200 grade silicon carbide paper (grit size $\sim 15\,\mu\text{m}$), quickly rinsed in an ultrasonic bath and dried before each run. Polishing the aluminium electrode using $5\,\mu\text{m}$ alumina powder had no significant effect on the results.

The electrolyte composition most commonly used was $0.8\,\text{M}\ ZnSO_4 + 1.07\,\text{M}\ H_2SO_4$. This composition was chosen as being representative of that used in 'low acid' ($\sim 100\,\text{g}\,\text{l}^{-1}$) zinc electrowinning processes. The electrolyte was deoxygenated by nitrogen sparging, since earlier work [17] had shown that dissolved oxygen causes a decrease in QE. Electrolytes were prepared from chemicals of analytical reagent grade or purer, plus either doubly distilled water or deionized water obtained from a MILLI-Q system (Millipore Corporation) fitted with an organic scavenger cartridge (Organex-Q). Various electrolytes were analysed *in situ* for trace impurities by ASV using long deposition times (up to 2 h) on a $\sim 2\,\text{cm}^2$ rotating glassy carbon electrode. Some electrolytes were also analysed by ICP to check for elements not detected by ASV.

The QE for zinc electrodeposition was determined as before [17], from the weight of zinc deposited at constant current after the passage of $\sim 600\,\text{C}$ ($\sim 200\,\text{mg}$ zinc). Where possible (generally with the aluminium cathodes), the zinc deposit was stripped from the electrode and weighed separately. In other cases, e.g. zinc deposited on zinc, lead or indium, the deposit adhered strongly and the difference in electrode weight before and after deposition was employed for the calculation. The current source was either a Keithley 225 constant current source or a PAR 173 Potentiostat/Galvanostat equipped with a PAR 179 Digital Coulometer. The QE could be estimated with a standard deviation of better than 0.2% and this precision was useful in detecting some of the smaller effects.

3. Results and discussion

3.1. *Electrolytes prepared from reagent grade zinc sulphate*

Initially, a series of electrolytes was prepared from various sources of reagent grade zinc sulphate and sulphuric acid. The QE for zinc electrodeposition was normally determined under the following set of conditions: rotating aluminium cathode; rotation rate (n rev s^{-1}), 20; current density (J), 400 A m^{-2}; deposition time (t), 120 min; temperature (T), 25° C. The results are summarized in Table 1. The varying QE values are presumed to reflect different impurity levels in the reagents. The electrolyte prepared using Merck AR $ZnSO_4 \cdot 7H_2O$ and BDH Aristar H_2SO_4 produced a relatively smooth zinc deposit with the highest QE, namely 97.6%; the water used to make up the solution (doubly distilled or MILLI-Q) had no effect on QE. Because of the favourable performance of this electrolyte and the availability of a quantity of a single batch of zinc sulphate, it was adopted as the 'baseline electrolyte' for subsequent comparisons of electrolyte preparation and purification methods.

Table 1. Coulombic efficiency obtained in electrolytes prepared from reagent grade zinc sulphate

Zinc sulphate	*Sulphuric acid*	*QE (%)*
BDH (Analar)	BDH (Analar)	95.7
Baker (Analysed)	BDH (Analar)	95.9
M & B (Pronalys)	BDH (Analar)	97.3
Merck AR	BDH (Analar)	97.5
Merck AR	BDH (Aristar)	97.6
Merck AR	Merck (Suprapur)	97.6

Table 2. Variation of coulombic efficiency with electrode rotation rate, current density and temperature

Variable	*Range*	*QE range (%)*
Rotation rate	4–64 s^{-1}	97.3–97.7
Current density	200–800 A m^{-2}	97.8–96.3
Temperature	25–45° C	97.6–98.2

3.2. *Effect of electrode rotation rate, current density and temperature*

The variations in QE for the baseline electrolyte with electrode rotation rate, current density and temperature were determined over limited ranges of each variable with the others held constant. Deposition time was changed with current density to give a constant charge passed. The results are shown in Table 2. While the range of variation observed in QE is smaller than observed for changes in reagents (see Table 1), all three deposition conditions are important in determining QE. Systematic variation of conditions to allow determination of maximum QE is reported below (see Section 3.6).

3.3. *Effect of deposition time and substrate*

Visual observation of gas bubbles formed during runs with aluminium substrates suggested that hydrogen was evolving at a greater rate at the beginning of zinc deposition. Therefore, electrolyses were run for varying times to quantify this effect on the measured QE; the results are shown in Fig. 1. The QE decreases with decreasing deposition time, confirming that more hydrogen is evolved (i.e. the CE is lower) in the initial stages of deposition. This is presumably a consequence of the partly exposed substrate during the early stages of zinc deposition.

QE measurements were therefore made on a range of substrates. These included lead, indium and glassy carbon, which are known to have high hydrogen overpotentials [18], and zinc, on which any time dependence of CE should be minimized. The results are summarized in Table 3. The range of QE observed is small, with glassy carbon and indium giving the best results. These observations indicate that the overall effect on QE of these substrates with high

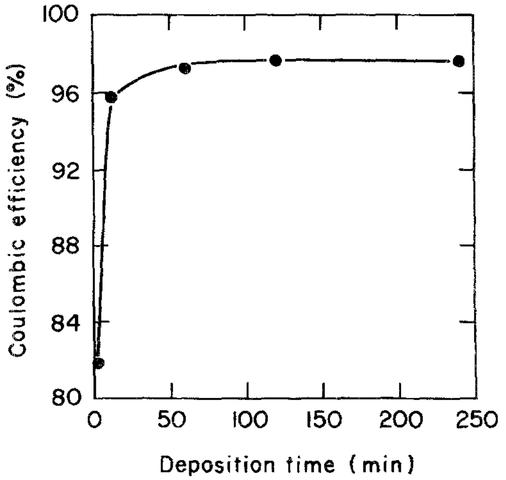

Fig. 1. Coulombic efficiency for zinc electrodeposition as a function of deposition time. Electrolyte, AR $ZnSO_4 \cdot 7H_2O$/BDH Aristar H_2SO_4; $2\,cm^2$ aluminium cathode; $n = 20\,s^{-1}$; $J = 400\,A\,m^{-2}$; $T = 25°C$.

hydrogen overpotentials is small and probably important only over the very early stages of deposition, before complete coverage by zinc is achieved.

The results in Fig. 1 allow estimation of a 'steady state' QE of 97.8–98.0% for the latter stages of deposition with the aluminium substrate now fully covered by zinc; at this stage hydrogen should evolve at a uniform rate. This estimate was supported by the measurements made on zinc itself (Table 3) where a QE of 97.9% was obtained over 2 h. Zinc is not a convenient substrate for routine QE determinations since the adherent deposit cannot be stripped, but measurements on zinc are clearly useful in obtaining an estimate of QE independent of the effects of a foreign substrate.

3.4. *Purification of the baseline electrolyte*

Several methods of purifying the baseline electrolyte were employed in attempts to improve QE from 97.6%. These involved purifying the starting reagents, a solution of the zinc sulphate or the acidified electrolyte itself. Details of the methods used are as follows.

(i) The sulphuric acid was purified by sub-boiling distillation using a unit based on a National Bureau of Standards design [19] which produced acid at $\sim 150\,ml\,h^{-1}$. This technique avoids the problems of solution creep and mist carry-over.

(ii) The AR zinc sulphate was recrystallized both once and twice from aqueous solution, with a yield of ~20%.

(iii) Zinc sulphate solution, slightly acidified (pH 2), was purified by cementation with either zinc dust or granules ($\sim 4\,g\,l^{-1}$ AR Zn, 1 h, 80–90°C). After filtering, the electrolyte was made up by adding the appropriate quantity of sulphuric acid.

(iv) The electrolyte itself was pre-electrolysed for 2 and 4 h at a set potential (−1.0 V versus SCE) using a $2\,cm^2$ glassy carbon electrode rotating at either 20 or $80\,rev\,s^{-1}$.

The values of QE obtained from the resultant purified electrolytes are summarized in Table 4. We immediately see the intriguing result that purification procedures either have no effect or lower the QE. The most obvious explanations of this behaviour are that the attempts at purification activate or concentrate a deleterious impurity or remove a beneficial impurity, probably originating from the zinc sulphate. Evidence presented in detail elsewhere [20] indicates that the latter mechanism is operating here; lead has been reported [2, 3] as having a beneficial influence on QE, and ASV analysis of the unpurified electrolyte revealed that it contained ~1.2 p.p.m. lead.

Table 3. Effect of substrate on coulombic efficiency

Substrate	*QE (%)*
Aluminium	97.6
Lead	97.6
Zinc	97.9
Indium	98.0
Glassy carbon	98.0

Table 4. Effect of purification of baseline electrolyte on coulombic efficiency

Purification method	*QE range (%)*
Nil	97.6
Distillation H_2SO_4	97.6
Recrystallization $ZnSO_4$	95.6–97.5
Zinc dust cementation	96.4–97.2
Pre-electrolysis	95.3–95.7

Table 5. Effect of reagent nominal purity on coulombic efficiency

Reagent	*Nominal purity (%)*	*QE range (%)*
$ZnSO_4 \cdot 7H_2O$ (Spex)	99.999	95.8
ZnO (Sharpe)	99.99	95.9
ZnO (Spex)	99.999	96.3
Zn (Koch-Light)	99.999	96.9–97.6
Zn (Koch-Light)	99.9999	96.9–97.4

3.5. *Electrolytes prepared from reagents of very high purity*

Since purification of a reagent grade electrolyte is not the pathway to an increase in QE, a range of electrolytes was prepared using commercially available $ZnSO_4 \cdot 7H_2O$, ZnO and Zn of high nominal purity (> 99.99%), plus BDH Aristar H_2SO_4. Zinc metal of such purity dissolves very slowly in sulphuric acid. Dissolution was accelerated by resting the zinc rod on a carefully cleaned platinum grid. Platinum contamination of the electrolyte under these conditions does not occur especially because the platinum remains cathodically protected by the zinc at all times. It is interesting to note that the platinum remains bright when used to dissolve 99.9999% zinc, but darkens for less pure grades, presumably due to a residue of those impurities which can co-deposit (cement) onto platinum at the zinc corrosion potential. The values of QE achieved for these electrolytes ranged from 95.8–97.6% and are summarized in Table 5; the use of distilled (sub-boiling) sulphuric acid did not affect QE.

To assess the purity of these electrolytes, some were analysed using ASV and others by ICP. Fig. 2 shows the anodic stripping voltammograms for two of the electrolytes from Table 5 compared with the baseline electrolyte (prepared using AR grade $ZnSO_4 \cdot 7H_2O$). The peaks at ~ −0.2, −0.5 and −0.8 V (versus SCE) were identified by standard addition to be due to copper, lead and cadmium, respectively. The lead peak on the voltammogram for the baseline electrolyte corresponds to 1.2 p.p.m. lead. ASV shows a substantial improvement in purity for electrolytes prepared from 99.999% and 99.9999% zinc. Some electrolytes (from Table 5) were also examined by ICP and the results are summarized in Table 6; for comparison, we include typical plant electrolyte data [21]. Again, the improvement in overall purity for the electrolytes prepared from the high-purity zinc is evident. Based on the available analytical techniques, the electrolyte prepared from 99.9999% zinc is confirmed as superior in overall purity. In addition, the QE for this electrolyte was unaffected by pre-electrolysis and had very

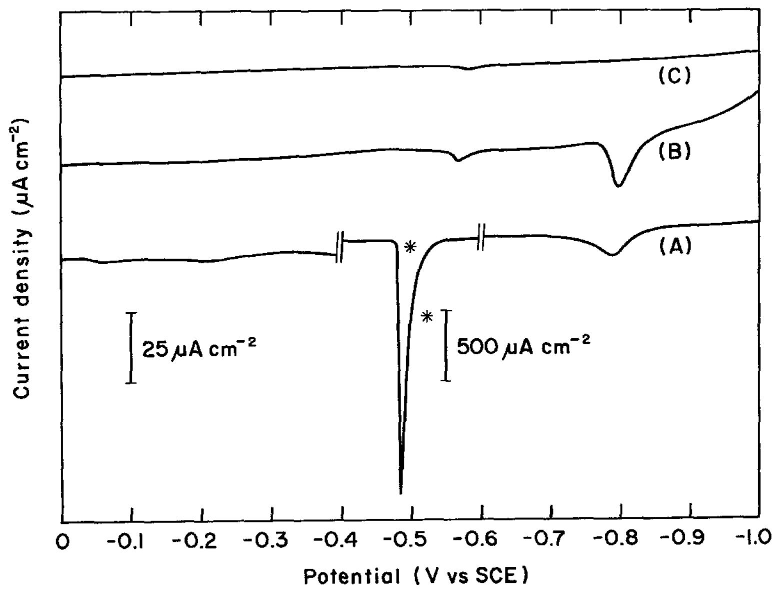

Fig. 2. Anodic stripping voltammograms on a 2 cm^2 glassy carbon electrode for electrolytes prepared from BDH Aristar H_2SO_4 and (A) AR $ZnSO_4 \cdot 7H_2O$, (B) 99.999% zinc, (C) 99.9999% zinc. Deposition conditions: 120 min at −1.0 V (versus SCE); n = 20 s^{-1}; T = 25°C. Stripping conditions: 1 mV s^{-1}; n = 20 s^{-1}; T = 25°C.

Table 6. ICP analyses of some zinc sulphate electrolytes (0.8 M $ZnSO_4$ + 1.07 M H_2SO_4). Impurity concentrations are given in p.p.m.

Element	*Merck AR* $ZnSO_4 \cdot 7H_2O$	*Spex 99.999%* $ZnSO_4 \cdot 7H_2O$	*Spex 99.999%* ZnO	*Koch-Light 99.999% Zn*	*Koch-Light 99.9999% Zn*	*Typical plant electrolyte [21]*
Cd	0.04	0.14	0.08	0.04	< 0.01	0.11
Co	< 0.02	0.06	< 0.02	< 0.02	< 0.02	0.029
Cu	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.073
Fe	< 0.05	< 0.05	0.09	< 0.05	< 0.05	10.3
Ni	0.21	0.06	0.03	< 0.02	< 0.02	0.025
Pb	1.4	0.7	1.0	< 0.1	< 0.1	0.75
Sn	< 0.01	0.04	< 0.01	< 0.01	< 0.01	–

little dependence on electrode rotation rate which would be expected to influence impurity deposition rates. These observations tend to support the assessment of a high degree of purity of this electrolyte.

While the electrolytes prepared from the two high-purity zinc grades gave the best QEs of this group (see Table 5), the QE of 97.6% achieved in the baseline electrolyte was never exceeded. The larger variability in the QE observed for these electrolytes (96.9–97.6%) compared with that for the baseline electrolyte (consistently 97.6%) may reflect quality variations in the zinc starting material or sensitivity to minor variations in impurity composition at these low levels.

It appears, then, that an improvement in electrolyte purity does not, in itself, guarantee an increase in QE. This is particularly so when comparing with an electrolyte containing a beneficial impurity such as lead, which seems to be ubiquitous in the usual laboratory zinc reagents. The steady increase in QE with purity of the starting materials reported by Znamenskii and Stender [12] was not observed here. However, it is difficult to make a meaningful comparison because of differences in electrodeposition conditions and the absence of comparable trace analytical data. An optimization process has been employed to ascertain whether the levels of QE (~99%) reported by Znamenskii and Stender [12] can be obtained with our electrolytes under any conditions; a summary of the relevant results of this work is given in the following section.

3.6. *The maximization of coulombic efficiency*

The QE results given in the previous two sections refer to a fixed set of electrodeposition conditions. Varying these conditions with a particular electrolyte gives some scope for improving the QE, as already seen in Section 3.2. To define the upper limit of QE for a particular electrolyte, several statistical methods are available [22, 23]. The one chosen here involved an approach to the upper limit via 'the path of steepest ascent' [22, 23]. The method is iterative in nature and, with sufficient data, allows the generation of surfaces showing QE as a function of electrodeposition conditions; the full details of the application of the method will be reported in a subsequent communication [24].

The electrolyte composition was kept constant (0.8 M $ZnSO_4$ + 1.07 M H_2SO_4) and the QE was optimized with respect to temperature,

Table 7. Optimal conditions for zinc electrodeposition

Electrolyte	*Optimal conditions*			*Maximum QE (%)*	
	T (°C)	*J* ($A m^{-2}$)	*n* (s^{-1})	*Al substrate*	*Zn substrate*
Baseline	35–50	400–500	35–50	98.5	98.8
99.9999% Zn	61	890	38	98.4	98.4

current density (constant total charge) and electrode rotation rate. Two electrolytes of different purities were examined in this way, namely (i) the baseline electrolyte which contains ~0.2 p.p.m. nickel and ~1 p.p.m. lead as the main impurities (Table 6), and (ii) the electrolyte of very high purity prepared from 99.9999% zinc. The conditions under which the QE reached a maximum are presented in Table 7. Maximum QE results are quoted for both zinc and aluminium substrates. With the baseline electrolyte the zinc substrate, as found previously (Section 3.3), gave a small increase in QE (from 98.5 to 98.8%). No such increase was found for the very-high-purity electrolyte (98.4%).

While the optimal conditions for QE are quite different for the two electrolytes, the maximum QE is similar. This result might not have been expected considering the different impurity compositions of the two electrolytes. The optimal conditions for the baseline electrolyte are similar to typical industrial practice (except for mass transfer rate), but the QE is some 8% higher. While the maximum QE obtained for the electrolyte of very high purity was 98.4%, this does not preclude the attainment of higher QEs in the presence of beneficial impurities such as lead, as observed for the baseline electrolyte. Of course, the electrolyte composition (zinc/acid ratio) could also be varied and this matter is examined in the final section.

3.7. *Effect of zinc and acid concentrations*

It is reasonable to expect QE to be some function of electrolyte composition (i.e. zinc sulphate and sulphuric acid concentrations). Wark [14, 15] has formalized a relationship between QE and the zinc/acid ratio ($[ZnSO_4]/[H_2SO_4]$) based on laboratory experiments, which has found some use in the industry [25]. Differences in electrolyte composition between zinc plants occur mainly as differences in sulphuric acid concentration. Therefore, in our investigation of the effect of the zinc/acid ratio on QE, under RDE conditions, the zinc sulphate concentration was held constant at 0.8 M. The electrolyses were conducted using the electrolyte of very high purity, prepared from 99.9999% zinc, and the optimal conditions presented in Table 7 were employed.

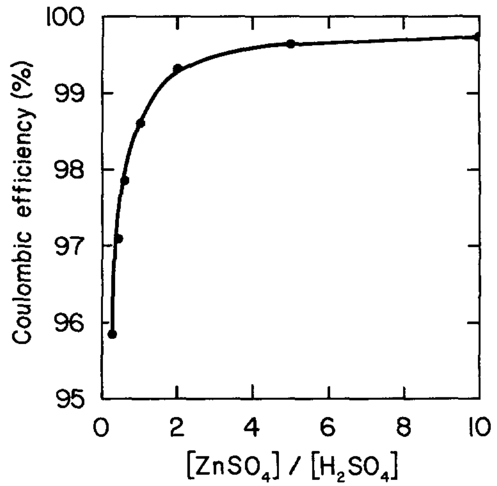

Fig. 3. Coulombic efficiency for zinc electrodeposition as a function of $[ZnSO_4]/[H_2SO_4]$. Electrolyte, 99.9999% zinc/BDH Aristar H_2SO_4; $2\,cm^2$ aluminium cathode; $n = 38\,s^{-1}$; $J = 890\,A\,m^{-2}$; $t = 53.9\,min$; $T = 61°C$.

The variation of QE with $[ZnSO_4]/[H_2SO_4]$ is shown in Fig. 3. The shape of the curve is similar to that observed by Wark [14, 15] and Fosnacht and O'Keefe [26]. Analysis according to 'Wark's rule', $QE/(100 - QE) = K[ZnSO_4]\,[H_2SO_4]$, is shown in Fig. 4. The fit is reasonable for $[ZnSO_4]/[H_2SO_4]$ in the range 0.3–2, with $K \simeq 73$. Wark's data [14, 15] gave $K \simeq 30$, but note that these experiments were conducted with constant total sulphate concentration and different electrodeposition conditions. The value of K could perhaps be considered an index of electrolyte performance – the higher, the better. Assuming that the optimal electrodeposition conditions are independent of bulk electrolyte composition, the data of Fig. 3 represent the best that can be obtained for a very-high-purity electrolyte of varying composition; apparently $QE \rightarrow 100\%$ only as $[ZnSO_4]/[H_2SO_4] \rightarrow \infty$ (i.e. a neutral solution).

4. Conclusions

Reagent grade chemicals used to prepare electrolytes contain sufficient impurities to affect QE; different sources of chemicals produce different QEs. The main source of impurities appears to be the zinc-containing reagent. The QE for zinc deposition at an RDE in an electrolyte prepared from AR grade $ZnSO_4$/BDH Aristar H_2SO_4 (the

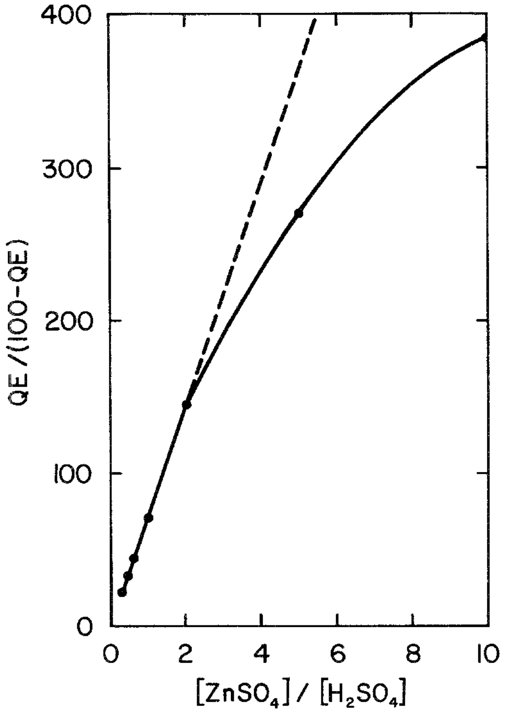

Fig. 4. Test of 'Wark's Rule'; plot of QE/(100 − QE) versus [$ZnSO_4$]/[H_2SO_4] for the data of Fig. 3. Electrolyte, 99.9999% zinc/BDH Aristar H_2SO_4; 2 cm^2 aluminium cathode; n = 38 s^{-1}; J = 890 A m^{-2}; t = 53.9 min; T = 61° C.

'baseline electrolyte') was found to be a function of temperature, current density and electrode rotation rate; deposition time had a minor effect at short times depending on the substrate. Attempts at increasing QE by purification of the baseline electrolyte failed, apparently because of removal of the beneficial influence of residual lead.

Electrolytes were also prepared from commerical reagents of high nominal purity (zinc metal, zinc oxide and zinc sulphate). The best electrolyte, as evaluated by ASV and ICP, was produced by dissolution of 99.9999% zinc in BDH Aristar H_2SO_4. The performance of this electrolyte was unaffected by pre-electrolysis and only to a minor extent by electrode rotation rate, consistent with its high purity. Neither the nominal purity of the reagents nor the assessed purity of the electrolyte (i.e. total detectable as measured by ASV and ICP) was a useful predictor of QE. We conclude that the QE in these solutions is still influenced by impurities either below detection limits or not sought in the analyses. Whether or not the QE could be further increased if a means could be found to lower these impurity levels remains undecided. A related question is: how much further can the hydrogen overpotential of the electrodeposited zinc be increased by making it purer?

The optimal electrodeposition conditions and, to a lesser extent, the corresponding QEs depended on which electrolyte was used and were presumably a function of electrolyte impurity content. The optimal value of QE found for an electrolyte of very high purity shows that *in principle* there is no bar to significant improvement in the QE (up to ~98%) of existing processes. However, the temperature (the dominant factor) and the hydrodynamic conditions required to achieve such high QEs are much different from industrial practice which is constrained (for many reasons) to a small range of operating conditions. The degree to which QE could be increased by improving electrolyte purity, raising the temperature, etc., will of course be determined by economics and other processing conditions (e.g. ore source).

The relationship between QE and zinc/acid ratio observed by Wark [15] is obeyed approximately in electrolytes of a very high purity over a limited range of composition, but this does include the typical operating range for most zinc plants ([$ZnSO_4$]/[H_2SO_4] of 0.5–0.75). Wark claimed that the relationship applied to high-purity electrolytes over long deposition times, but only to the initial stages of zinc electrodeposition for less pure electrolytes [15]. In any case, values of QE approaching 100% may be obtained only as [$ZnSO_4$]/[H_2SO_4] $\rightarrow \infty$. However, this does not preclude the possible improvement of QE for an electrolyte of a given composition by the addition of appropriate beneficial additives.

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