

The estimation of the coulombic efficiency of zinc electrodeposition by measurement of current efficiencies at a rotating ring disc electrode

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The rotating ring disc electrode (RRDE) offers a simple method for the determination of the current efficiency (CE) of zinc electrodeposition in acidic zinc sulphate electrolytes. The hydrogen evolved during zinc deposition can be detected at the ring. This allows estimation of the current due to hydrogen formation at the disc and hence CE for electrodeposition of zinc can be calculated. Investigations of the conditions under which reliable measurements of CE can be obtained are described. A correlation between CE, determined using the RRDE, and the coulombic efficiency (QE), determined by weighing the zinc deposit obtained after 2 h electrodeposition at constant current, is established for a range of electrolyte compositions. It is suggested that measurement of CE at a Pt–Zn RRDE provides an efficient means of estimating QE for zinc electrolytes.

1. Introduction

Recent studies of coulombic efficiencies (QE) in zinc electrowinning in these laboratories [1] highlighted the need for a fast and reliable method for estimating QE. The method used in that work involved the electrodeposition of zinc for 2 h under galvanostatic conditions onto a rotating aluminium cathode; the zinc deposit was stripped and weighed to determine QE. While this method is very precise, it is extremely tedious and a faster alternative would be desirable. Methods developed earlier depend on anodic dissolution of the zinc deposit [2–4], or measurement of the total volume of hydrogen evolved or the rate of hydrogen gas evolution during zinc electrodeposition [5–8].

The rotating ring disc electrode (RRDE) offers a simple means for determining the instan-

taneous current efficiency (CE) of electrodeposition through measurement of the ring current for the oxidation of hydrogen evolved from the disc as a function of the total disc current. Provided experimental conditions can be found under which CE determined using the RRDE correlates closely with QE for electrolytes of practical interest in zinc electrowinning, application of the RRDE to this problem should lead to a rapid and reliable method of assessing likely electrolyte performance.

There have been several accounts of the detection of dissolved gases by RRDE [9–12]. In a recent review, Bruckenstein and Miller [9] mentioned the detection of hydrogen evolved during copper electrodeposition using a Pt–Pb RRDE. Khomskaya and Kolosov [10] estimated the supersaturation of oxygen in KOH solutions using a Cd–Ni RRDE. Both Ludwig *et al.* [11]

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and Untereker [12] used a Pt–Pt RRDE to detect hydrogen evolved in acidic solutions.

In this paper we report a method for the estimation of QE in zinc electrowinning from the instantaneous values of CE determined with a Pt–Zn RRDE.

2. Experimental details

A conventional three-compartment glass electrochemical cell, containing a saturated calomel electrode (SCE) as reference and a gold wire counter electrode, was used. A Pine Instrument Company Model DT6 Au–Au RRDE ($r_1 = 0.382$, $r_2 = 0.399$, $r_3 = 0.422$ cm) with a disc area of 0.458 cm^2 was rotated by a Model ASR 2 Electrode Rotator. After the electrode was polished with $5 \mu\text{m}$ Al_2O_3 powder, the collection efficiency for the ferricyanide–ferrocyanide couple, determined using freshly prepared 0.005 M $\text{K}_3\text{Fe}(\text{CN})_6$ in 0.1 M Na_2SO_4 , was found to be 0.168 for rotation rates from 1000 to 6000 r.p.m. The theoretical collection efficiency for this ring–disc geometry interpolated from the data of Alberly and Bruckenstein [13] is 0.177.

Gold is an indifferent electrocatalyst [14] and no potential could be found at which hydrogen oxidation in H_2SO_4 was mass transport controlled on the ring. The ring was platinized, therefore, using $\sim 2 \text{ wt } \%$ H_2PtCl_6 in 1 M HCl , at -0.2 V versus SCE, as described by Cathro [15]. Because the platinum deposit grows in three dimensions, the ring–disc gap after platinizing the ring is a function of the thickness of this deposit. Values of collection efficiency could be varied from 0.17 to 0.21 depending on the deposition time.

Zinc electrolytes were prepared from AR $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ or ZnO , BDH Aristar H_2SO_4 and double-distilled water or deionized water (Milli-Q System) [1]. The electrolyte composition used in most of the work was 0.8 M $\text{ZnSO}_4 + 1.07 \text{ M}$ H_2SO_4 which is typical of electrolytes in ‘low acid’ ($\sim 100 \text{ g l}^{-1}$) zinc electrowinning processes. For measurement of high CEs a composition of 0.8 M $\text{ZnSO}_4 + 10^{-2} \text{ M}$ H_2SO_4 was used. The reduction of dissolved oxygen at the electrode surface causes a decrease in CE, as shown by Biegler and Swift [16], and all elec-

trolytes were, therefore, deaerated with high purity nitrogen gas further deoxygenated by passage over copper powder on kieselguhr at 200°C . To prevent ingress of air through the open annulus around the RRDE a stream of nitrogen was passed over the surface of the solution during all measurements.

The potentiostat and ring-potential controller were constructed in these laboratories. Current–potential outputs were recorded using a Hewlett-Packard Model 7046A X–Y recorder. All experiments were conducted at room temperature ($\sim 23^\circ \text{C}$). Potentials quoted in this paper are given with respect to the SCE.

3. Results and discussion

3.1. Detection of hydrogen in 1 M H_2SO_4

The method of measuring CE in zinc electrolytes depends on the assumption that the anodic ring current observed is a constant proportion of the current due to hydrogen production at the disc. Since the only other process that can occur at the disc in deoxygenated zinc electrolyte is deposition of zinc, the ratio of ring current to disc current gives a measure of CE. The lower limit of CE of zinc electrodeposition that can be measured reliably by the RRDE technique will be determined by the point in the plot of ring current versus hydrogen disc current where curvature becomes apparent. Ludwig *et al.* [11] noted a reduction in the collection efficiency of the ring at high rates of hydrogen evolution due to bubble formation. Since the hydrogen disc current is not directly measurable in zinc electrolyte, the performance of the RRDE system was investigated in 1 M H_2SO_4 to establish the range of CEs of zinc electrodeposition that might be covered by the RRDE method.

A plot of ring current (I_r) versus disc current (I_d) for the Pt–Au RRDE is shown in Fig. 1. The ring potential was set at 0.4 V , well into the mass transport limited region for hydrogen oxidation. The general behaviour is similar to that observed by Khomskaya and Kolosov [10] for oxygen in KOH solutions. For rotation rates from 1000 to 4000 r.p.m., constant collection efficiencies were observed for disc currents up to $600 \mu\text{A}$ (1.3 mA cm^{-2}). The break from linearity

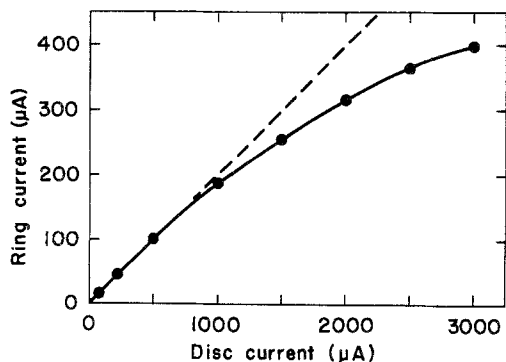


Fig. 1. Plot of disc current versus ring current for Pt-Au RRDE in 1 M H_2SO_4 ($E_r = +0.4\text{ V}$, rotation rate = 1200 r.p.m.).

observed in Fig. 1 is probably associated with the formation of hydrogen gas bubbles at the disc. Transport of the hydrogen in these bubbles (from the disc to the ring) will occur through diffusion rather than hydrodynamic flow and will consequently be substantially slower than for dissolved hydrogen. Thus, the apparent collection efficiencies at high disc currents are lower than the theoretical value. The evolution of sufficient gas at the disc can cause a turbulent mass transfer regime which also would lead to a decrease in collection efficiency [17].

From Fig. 1 it would appear that the RRDE used in this work is capable of providing reliable measurements of CEs for hydrogen ring currents less than around $150\ \mu\text{A}$. Assuming that the linear region in Fig. 1 is limited by the onset of bubble formation, it seems likely that the upper limit for hydrogen ring current would be influenced strongly by the solubility of hydrogen in the relevant electrolyte solution, although it is known [10, 18, 19] that supersaturation of electrolyte near the electrode does occur during evolution of gas from an electrode. The solubility of hydrogen in 1 M ZnSO_4 is known to be significantly less than that in 1 M H_2SO_4 at room temperature [20]; data for the relative solubility of hydrogen in the $\text{ZnSO}_4\text{-H}_2\text{SO}_4$ electrolyte used in this work were therefore required to estimate the practical upper limit of I_r . The limiting currents for hydrogen oxidation at a platinum RDE were determined in 1 M H_2SO_4 and $\text{ZnSO}_4\text{-H}_2\text{SO}_4$ solutions saturated with hydrogen gas. These values, corrected according to the Levich equation for the different viscosities and

densities of the two solutions, show that the hydrogen solubility in the acidic zinc electrolyte is 74% of that in 1 M H_2SO_4 . In the light of this result it would appear that the upper limit of I_r for use in measurements of CE in zinc solutions should be about $100\ \mu\text{A}$.

Because I_r is directly proportional to the difference between the measured CE and 100%, it can provide an accurate measure of CE up to very high levels. The smallest value of I_r detectable with this system was $0.1\ \mu\text{A}$. This corresponds to a maximum measurable CE greater than 99.99% at disc current densities close to those used in practice ($40\ \text{mA cm}^{-2}$). Using $100\ \mu\text{A}$ as the upper limit for the reliable measurement of I_r , the lowest measurable CE would be 97.5% if the same disc current density were to be used.

3.2. Response of the RRDE in acidic zinc sulphate electrolyte

The optimum conditions for the measurement of CE in zinc electrodeposition using the RRDE were established with an electrolyte 0.8 M in ZnSO_4 and 1.07 M in H_2SO_4 . Zinc was plated onto the gold disc from 0.8 M ZnSO_4 ($20\ \text{mA cm}^{-2}$ for 20 min) prior to measurements in the acidic electrolyte in order to minimize difficulties during the initial stages of zinc plating due to the generation of excessive amounts of hydrogen on the gold substrate. The plot of I_r versus I_d for this Pt-Zn RRDE is shown in Fig. 2. The positive intercept on the ring current axis at zero disc current is due to formation of hydrogen through corrosion of zinc in the acid electrolyte.

The apparent CE for zinc electrodeposition at any point in this plot is given by

$$\text{CE} = \left[1 - \frac{I_r}{I_d} \times \frac{1}{N} \right] \times 100 \quad (1)$$

where N is the collection efficiency of the RRDE. CE gives a measure of the relative rates of hydrogen production and zinc deposition at the electrode potential applying at any value of disc current density, and consequently it would be expected that CE would vary with disc current density. The curvature of the plot in Fig. 2 for I_d up to about 12 mA is consistent with

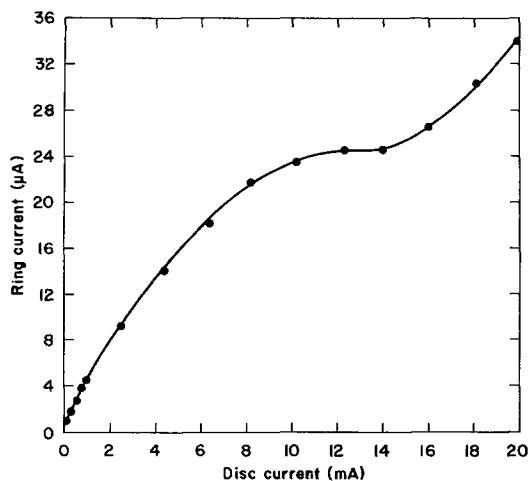


Fig. 2. Plot of disc current versus ring current for Pt-Zn RRDE in 0.8 M ZnSO_4 -1.07 M H_2SO_4 ($E_r = 0.4$ V, rotation rate = 1200 r.p.m., $N = 0.21$).

expectations from the literature [21, 22] and indicates an increase in the relative rate of zinc deposition (i.e. in the CE) as the electrode potential becomes more negative. It is difficult, however, to predict the exact relationship expected for this plot on the basis of published data [23] as there is evidence [24-26] of interaction between the zinc and hydrogen deposition reactions. At the higher I_d in Fig. 2 interpretation of the results is complicated by changes in the geometry of the RRDE within the time scale of the measurements. In particular there is a tendency for the gap between the disc and the ring to close and the sudden increase in I_r for I_d above about 14 mA is probably the result of the consequential increase in collection efficiency.

3.3. The correlation between current efficiency and coulombic efficiency

The QE for zinc electrodeposition measured by the method in [1] is linked to average CE over the deposition time (~ 2 h). CE does not remain constant over this period due to substrate effects during the initial stages of plating and subsequently to changes in electrolyte composition over the long period of the measurement. Consumption of zinc causes a small decrease in the zinc-acid ratio and depletion of metal impurities in the electrolyte causes a continuous variation in the composition of the zinc deposited. Since

the rate of hydrogen evolution is a sensitive function of the surface composition, CE would be expected to be strongly time-dependent. For these reasons it is not possible to estimate QE simply by measuring CE at disc current densities close to those used in practice (40 mA cm^{-2}). It is necessary to choose conditions of disc current density which provide a reliable and convenient measure of CE and to establish the correlation between CE and QE for a range of electrolytes so that an empirical relationship can be derived between these variables.

The disc current density chosen for these measurements should satisfy three criteria. It should be in a region where the measurement of CE itself is reliable. Ideally curvature of the plot in Fig. 2 should be low at that current density so that small errors in setting the current would have minimal effect on the value observed for CE. Finally, a wide range of CEs should be accessible at the disc current density chosen. For the RRDE used in this work an I_d of 1 mA (2.2 mA cm^{-2}) fulfils these requirements. Using this value for I_d and the maximum value of hydrogen ring current derived in Section 3.1, CEs down to 50% can be measured and hydrogen can be detected at the ring at a current equivalent to a CE of 99.9%. High values of disc current, closer to the current densities used in practice, are unsuitable because of the unfavourable effects of changes in the geometry of the RRDE during a measurement and because of the limited range of CE amenable to measurement.

To investigate the correlation between CE at a disc current density of 2.2 mA cm^{-2} and QE determined from the weight of zinc deposited, measurements were made for a series of electrolytes of different purities for which QE was known from earlier work [1]. Before these measurements the gold ring was cleaned and freshly platinized. After this treatment, the collection efficiency of the Pt-Au RRDE for hydrogen was measured in 1 M H_2SO_4 , giving a value of 0.172 which was used in all subsequent work. The gold disc was plated with zinc in 0.8 M ZnSO_4 for 2 min at 20 mA cm^{-2} , and for a further 2 min at the same current density in the particular electrolyte to be investigated.

Fig. 3 shows the plot of CE at 2.2 mA cm^{-2}

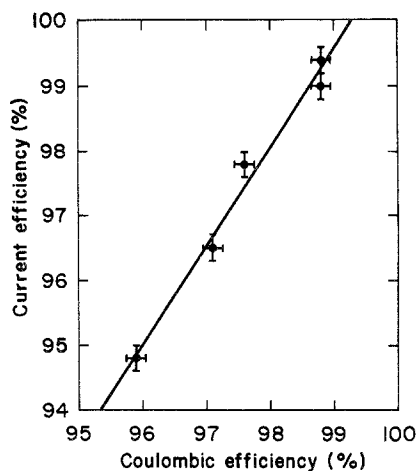


Fig. 3. Plot of coulombic efficiency determined by zinc weight versus current efficiency determined by Pt-Zn RRDE ($E_r = +0.4$ V, rotation rate = 1200 r.p.m., $N = 0.172$).

versus QE for five different electrolytes. Over the range of QE investigated, the relationship fits a straight line,

$$CE = -51.4 + 1.53QE \quad (2)$$

with a correlation coefficient of 0.99. Using the limits for reliable measurement of CE indicated above, Equation 2 implies that the RRDE can be used, with an I_d of 1 mA, to estimate QE values from 67% to 99%.

4. Conclusions

The measurement of CE at an RRDE offers an efficient means of estimating QE for zinc electrodeposition in zinc sulphate electrolytes. Although the present results cover only a narrow range of QE (96–99%), the practical range of QE (88–93%) lies well within the limits derived from Equation 2 for the reliable estimation of QE. It is reasonable to expect, therefore, that this technique should be applicable to the range of QE encountered in industrial electrolytes. It must be emphasized, however, that the RRDE technique is not an absolute method for the determination of QE, and calibration is necessary before advantage can be taken of the speed and simplicity of this approach. This requirement is especially important over an extended range of QE or if there is

any reason to suspect a change in the mechanism of hydrogen or zinc deposition in the range of electrolytes of interest.

The method is very promising and with further development should be applicable to other metal deposition processes where hydrogen is the byproduct. Improvement in the present case could be made by changing the RRDE materials (e.g. to Pt-Al) and the RRDE geometry. A wider ring-disc gap would moderate the effect of deposit growth on collection efficiency. A wider ring could be employed to compensate for the consequent loss of collection efficiency. No attempt has been made here to optimize the thickness of the initial metal deposit on the disc and to determine its effect on the real collection efficiency.

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