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The chronopotentiometric method for measuring the kinetics of metal dissolution and cementation reactions*

J. ZHENG, M. KHAN, S. R. LA BROOY, I. M. RITCHIE,‡ P. SINGH

A. J. Parker Cooperative Research Centre for Hydrometallurgy, School of Mathematical and Physical Sciences, Murdoch University, Western Australia 6150

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The validity of the chronopotentiometric method, which has been used for studying the kinetics of metal dissolution and cementation (displacement) reactions was examined. Using the dissolution of electrodeposited zinc films as an example, results are presented for the dissolution in a triiodide solution, in an acid solution and in an acidified triiodide solution. The effect of the substrate electrode, on which the zinc film is deposited, was found to be negligible in the case of the triiodide dissolution reaction which is known to be diffusion controlled. However, the substrate electrode can have a profound effect on the dissolution in acid, a reaction which is known to be chemically controlled. In addition, the apparent dissolution rate in acidified triiodide solutions can be greater than the sum of the separate dissolution rates. Explanations for these findings, based on the catalytic effect of the substrate electrodes, are presented. The applicability of the chronopotentiometric method to the cementation of copper (II) on to electrodeposited zinc films was also investigated. Similar difficulties to those found with the zinc/acidified triiodide system were encountered. As a result of the understanding of the pitfalls of the chronopotentiometric method developed in this work, it was possible to review critically previous measurements of this type, which have been reported in the literature. It was concluded that, while the majority of previous studies are correct, a serious error has been made in one paper.

1. Introduction

A common technique for determining the rate of a metal dissolution reaction is to sample the reactant solution periodically and then analyse the samples for the concentration of reactant or the amount of metal dissolved or both. A similar approach is often used to study the kinetics of a cementation reaction in which the ions of a less reactive metal are displaced from solution by a more reactive metal. A good example of this latter type of reaction is the displacement of gold from alkaline cyanide solution using zinc metal. Unfortunately, the technique of taking samples and analysing them tends to be slow. If the concentration changes are small, the measurements also lack precision.

In 1973, a much quicker and more precise method of measuring the rate of metal dissolution reaction was devised by Barth, Gans and Knacke [1]. This method depends on measuring the rate of loss of metal using chronopotentiometry. A known amount of the metal whose dissolution rate is being investigated is first plated onto an inert electrode. When the plated electrode is placed in the reactant solution, and its potential recorded relative to a reference electrode, the measured potential is the mixed potential characteristic of the metal dissolution. This mixed potential is maintained until all the metal which had been plated onto the inert electrode has been consumed. At this point, the potential of the inert electrode rises rapidly to some equilibrium potential. A typical chronopotentiogram is shown in Fig. 1. The dissolution rate, r, is simply calculated from the equation

$$r = \frac{\eta I_p t_p}{nFAt_d} \tag{1}$$

where η is the plating efficiency, I_p is the plating current, t_p is the plating time, n is the number of electrons transferred in the plating reaction, F is the Faraday constant, A the electrode area and t_d the dissolution time measured from the chronopotentiogram.

Since the original work of Barth, Gans and Knacke [1], the chronopotentiometric method has been used to study the kinetics of a number of dissolution and cementation reactions. These include the dissolution of copper in acidified acetonitrile/water mixtures [2], the displacement of copper (II) ions by iron [3], the displacement of copper (II) ions by zinc [4] and the displacement of gold (I) ions from an alkaline cyanide solution by zinc [5]. In all these studies, the validity of the technique has not been questioned. In this paper, the effect of the so-called inert electrode on a typical diffusion-controlled reaction (the dissolution of zinc by iodine) and a typical chemically controlled reaction (the dissolution of zinc in acid) will be investigated. In addition, the applicability of the chronopotentiometric method to measuring the rate

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‡ Author to whom correspondence should be sent.

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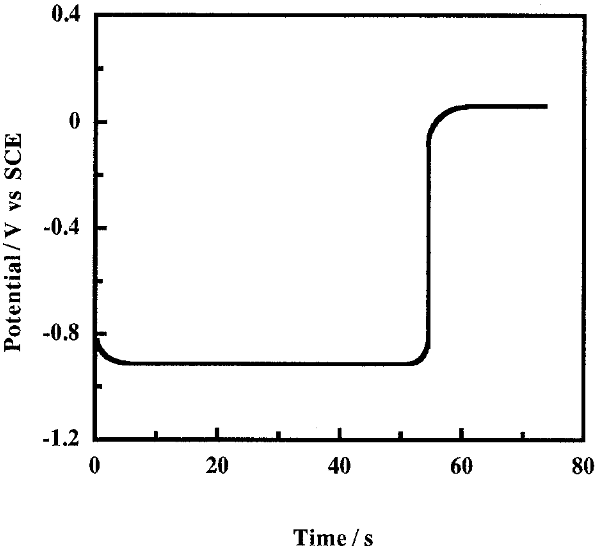

Fig. 1. Chronopotentiogram of Zn dissolution from 0.010 M I_2 in 0.50 M KI solution.

of cementation reactions will be considered. As will be shown, the results obtained using this technique must be interpreted with care. Previous studies using the chronopotentiometric method are reviewed in the light of this knowledge.

2. Experimental methods

All solutions were prepared from AR grade chemicals and Millipore Milli-Q water. The zinc plating solution contained 1.0 M zinc sulphate, 0.50 M sodium sulphate and 10 g dm^{-3} dextrin with a pH of about 4. It is based on a formulation reported by Isserlis [6]. Three types of stripping solutions were used: 0.010 M iodine in 0.50 M potassium iodide at pH 4.5; 0.040 M hydrochloric acid in 0.50 M potassium iodide; and 0.04 M hydrochloric acid and 0.010 M iodine in 0.50 M potassium iodide. Both the plating and the stripping solutions were maintained at 25.0 ± 0.2° C during the course of the experiments.

It was found that oxygen had to be rigorously excluded from the plating, wash and stripping solutions since it caused corrosion of the zinc films, particularly when platinum was used as the substrate electrode. To remove oxygen from the solutions, high purity argon gas was bubbled through them for a minimum of twenty minutes. After the solutions were degassed, they were maintained under an argon atmosphere for the duration of the experiment.

Because some of the reactions considered here are diffusion-controlled, the kinetic measurements were carried out using a rotating disc electrode which ensures reproducibility of the hydrodynamics.

The rotating disc apparatus used for both the plating and dissolution parts of the experiment was that described by Power *et al.* [7]. The diameters of the platinum and gold electrodes were 2.90 and 3.00 mm, respectively. In the ring-disc electrode experiments, a gold ring, gold disc system was used. The relevant diameters are: disc 3.0 mm; inner ring 3.5 mm; outer ring 5.5 mm. Prior to each experiment, the electrodes were successively polished using 500, 1200 and 2400 silicon carbide paper, and then rinsed thoroughly in deionised and Millipore water. The zinc films used in this study were deposited galvanostatically using a PAR 273 potentiostat/galvanostat. The standard plating conditions were 0.500 mA for 100 s at a disc rotation speed of 200 rpm.

After plating, the zinc films used in the dissolution studies were rinsed thoroughly and then transferred to the stripping cell. These operations were carried out quickly in order to minimize oxygen contamination. The chronopotentiograms were recorded using a Rikadenki R-02 chart recorder in conjunction with a PAR 173 potentiostat operating in the measuring mode. All potentials were recorded relative to a saturated calomel electrode.

The plating efficiency for zinc deposition was determined chronopotentiometrically. After depositing for 100 s, the plating current was reversed, thus causing the zinc film to dissolve anodically. While zinc metal remains on the so-called inert electrode, the dissolution potential remains approximately constant. But when all the zinc is dissolved, the electrode potential increases rapidly in a similar way to that shown in Fig. 1. The time, t_s, between the reversal of the current and the sharp increase in potential is then related to the current efficiency by

$$\eta = (t_s/100) \qquad (2)$$

Errors are reported as standard errors i.e. two standard deviations or 95% confidence limits.

3. Results and discussion

A typical chronopotentiogram for the dissolution of zinc in 0.04 M iodine/0.5 M iodide solution is shown in Fig. 1. As can be seen, it consists of an initial potential plateau corresponding to the mixed potential, followed by a sharp potential rise to a second plateau. The reaction time was taken to be the time at the potential half way between the two plateaux. Since the potential rise is very rapid, other definitions of the end point of the reaction do not make a significant difference to the calculated reaction rate.

Before the reaction rate can be calculated from Equation 1, the plating efficiency for the deposition of zinc on both platinum and gold must be determined. Using Equation 2, and averaging over five measurements, the plating efficiency on platinum was found to be 0.898 ± 0.036 and that on gold, 0.916 ± 0.005. Thus, within the limits of experimental error, the plating efficiency on the two electrodes are the same. It might have been expected that the plating efficiency for zinc on platinum would be less than that for zinc on gold. This is because more hydrogen would have been evolved on the platinum electrode than on the gold electrode, at least until the electrode surface had been covered with zinc which largely shuts off proton reduction on the noble metal electrode. However, any difference in plating efficiency between the

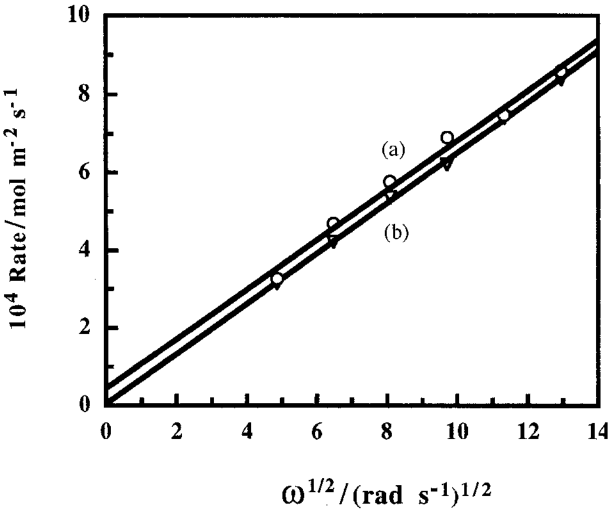

Fig. 2. Dissolution of zinc from solution: 0.010 M I_2, 0.50 M KI, pH 4.5. Curves: (a) Pt electrode; (b) Au electrode.

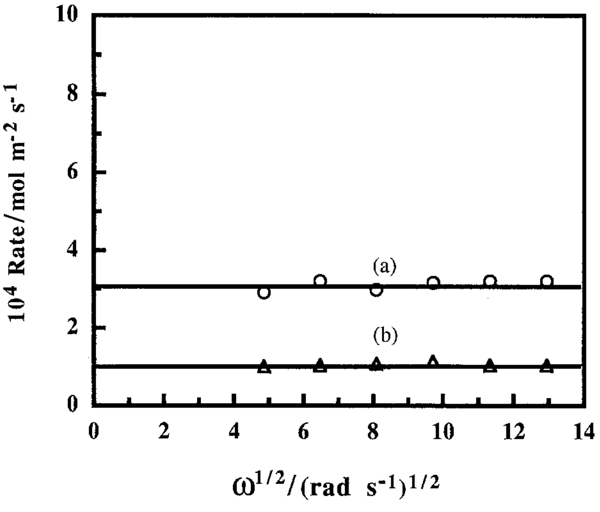

Fig. 3. Dissolution of zinc from solution: 0.040 M HCl, 0.50 M KI. Curves: (a) Pt electrode; (b) Au electrode.

two electrodes is masked by the large scatter in the results for the platinum electrode. This scatter might be due to differences in the preparation of the electrode surface which materially affect the activity of the surface towards hydrogen evolution.

Plots of the reaction rate, calculated from Equation 1 using the appropriate values of the plating efficiency, are shown in Fig 2 as a function of the square root of the disc rotation speed for both the platinum and gold electrodes. As expected for a diffusion controlled reaction [8], both plots are linear. Furthermore, the slopes of the two lines agree within the limits of experimental error, that for the platinum electrode being $(6.39 \pm 0.61) \times 10^{-5}$ mol m^{-2} s^{-1} rad$^{-1/2}$, and that for the gold electrode being $(6.47 \pm 0.15) \times 10^{-5}$ mol m^{-2} s^{-1} rad$^{-1/2}$. These values do not include the error in the plating efficiency since a similar error has already been incorporated as part of the rate measurements themselves.

The reason why the slopes of the lines are so similar is that the oxidizing agent, iodine in iodide solution, is reduced at the same rate on the part of the electrode surface which is covered with zinc metal as it is on the part of the electrode surface which is not covered with zinc metal. This is a characteristic of a diffusion controlled reaction. Thus the results are independent of the quality of the zinc layer; an ideal isotropic zinc film with no holes in it will dissolve at exactly the same rate as a zinc film with holes in it which expose the underlying platinum or gold electrode. At a rotating disc, we are only concerned with the geometric area of the electrode.

However, the nonzero intercept shown in Fig. 2 for the zinc-plated platinum electrode is not expected for a diffusion controlled reaction. It suggests that some chemically-controlled dissolution process is occurring in parallel with the iodine diffusion-controlled process. This chemically-controlled dissolution reaction is most likely that due to traces of oxygen left in solution. Certainly, the intercept increases in magnitude if special precautions to exclude oxygen are not taken. This is only a problem when the platinum electrode is used. Apparently gold is not a sufficiently good catalyst for the current due to oxygen reduction to be significant.

The slopes, $(r/\omega^{1/2})$, calculated from Fig. 2 and the plating efficiencies may be compared with those predicted from the Levich equation [8]

$$r/\omega^{1/2} = 0.62 D^{2/3} \nu^{-1/6} C \qquad (3)$$

where ω is the disc rotation speed, D is the diffusion coefficient of the oxidant species, ν is the kinematic viscosity of the reactant solution and C is the oxidant concentration. In an iodine/iodide solution, both iodine and triiodide ions can be present, according to the equilibrium equation.

$$I_2 + I^- = I_3^- \qquad (4)$$

The equilibrium constant for Equation 4 has been reported as being equal to $\log K_1 = 2.86$ M^{-1} at 25 °C [9]. Under these circumstances, the iodine is virtually all present as the triiodide ion. According to Gregory and Riddiford [10], the diffusion coefficient of the triiodide ion is 11.5×10^{-10} m^2 s^{-1}. The kinematic viscosity of a 0.50 molal solution of potassium iodide is, from the data of Out and Los [11], 0.885×10^{-6} m^2 s^{-1}. The concentration difference between a 0.5 molal solution and a 0.5 molar solution is only 0.3% and so it seems reasonable to assume that the corresponding change in kinematic viscosity is also very small, particularly since it only enters the Levich equation as the minus one sixth power. Substituting these figures into Equation 3 gives a value for the slope, $(r/\omega^{1/2})$ of 6.9×10^{-5} mol m^{-2} s$^{-1/2}$ rad$^{-1/2}$. This is in reasonable agreement with the values determined experimentally in the present study.

Figure 3 shows the results for the acid dissolution of zinc films deposited on platinum and gold electrodes. The behaviour is quite different to that of the iodine/iodide dissolution reaction. First, there is no dependence on disc rotation speed indicating that the reaction is chemically controlled. Secondly, the dissolution rates depend markedly on the substrate electrode, that for platinum being (31.1 ± 1.3)

$\times 10^{-5}\,\mathrm{mol\,m^{-2}\,s^{-1}}$ and that for gold being $(10.6 \pm 0.5) \times 10^{-5}\,\mathrm{mol\,m^{-2}\,s^{-1}}$.

The reason for this difference is that the zinc films are not perfect, but are porous or become porous during the dissolution process. Consequently, the inert electrode is exposed, creating the conditions for bimetallic corrosion [12]. The corrosion reaction here can be considered to be made up of two half reactions: the oxidation of zinc

$$\mathrm{Zn} \longrightarrow \mathrm{Zn^{2+}} + 2\mathrm{e^-} \qquad (5)$$

and the reduction of hydrogen ions to give hydrogen gas

$$2\mathrm{H^+} + 2\mathrm{e^-} \longrightarrow \mathrm{H_2} \qquad (6)$$

The second of these two half reactions is relatively slow on zinc since hydrogen ion reduction has a low standard exchange current density on this metal in acidic solutions [13]. However, hydrogen ion reduction is rapid on platinum [13] and so if zinc is connected to platinum electrically, hydrogen ion reduction occurs on the platinum and the dissolution of zinc proceeds more rapidly than it would if not connected to the platinum. Thus it can be seen that platinum is catalysing the dissolution rate of zinc. Gold has a similar effect, but since the standard exchange current density for hydrogen ion reduction on gold is lower than for platinum (but higher than that for zinc [13]), the effect on the dissolution rate of zinc is expected to be less than that for platinum. This is consistent with the results shown in Fig. 3.

When zinc films deposited on platinum are dissolved in a solution containing both iodine/iodide and hydrogen ions, the results shown in Fig. 4 are obtained. One might have expected that the rate of dissolution of zinc in iodine/iodide solutions containing acid would be the sum of the two dissolution reactions proceeding independently. However, this is not the case. Experimentally, the reaction of zinc with iodine and hydrogen ions proceeds at a faster rate than the sum of the two separate reactions. Since this synergism is not observed when a gold electrode is used, it is thought to be due to the fact that the iodine dissolution reaction is opening or widening holes in the zinc film, thereby making more platinum surface available to catalyse the hydrogen ion reduction reaction. Under these circumstances, it is clearly not possible to determine the rate of dissolution of zinc in iodine plus acid, and then subtract the rate of dissolution of zinc in iodine to obtain the rate of dissolution of zinc in acid.

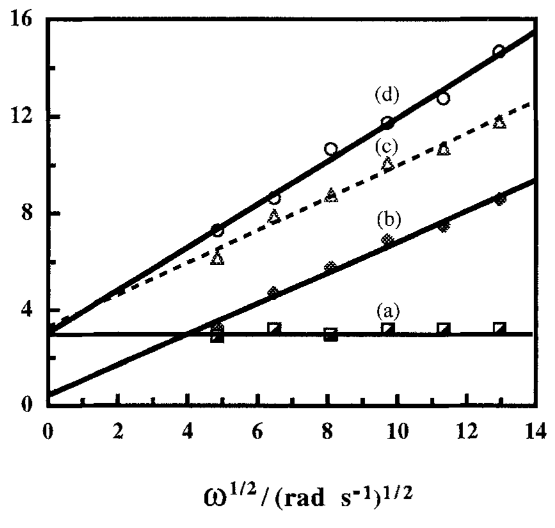

Fig. 4. Dissolution of zinc from Pt substrate electrode in solution. Curves: 9a) 0.040 M HCl, 0.50 M KI; (b) 0.010 M $\mathrm{I_2}$, 0.50 M KI, pH 4.5; (c) curve (a) + curve (b); (d) 0.010 M $\mathrm{I_2}$, 0.040 M HCl, 0.50 M KI.

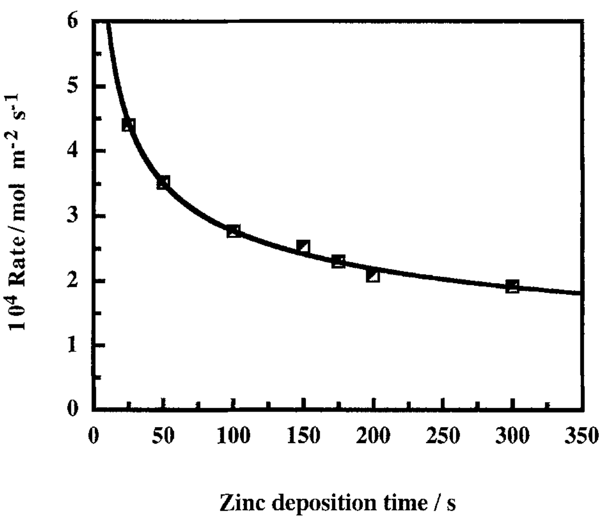

Fig. 5. Effect of thickness of Zn film on Zn dissolution rate from Pt electrode.

A corollary of the above finding is that the apparent rate of dissolution of a zinc film on a platinum electrode will depend on the thickness of the zinc film deposited. This is shown in Fig. 5. When the zinc deposition time is short, the zinc film is relatively discontinuous, allowing the hydrogen ions to make contact with the underlying platinum which catalyses their reduction. The apparent reaction rate is therefore high. On the other hand, when the zinc film is thick, hydrogen ions cannot be reduced on the platinum electrode, at least not until the film has been partially dissolved, and so the apparent reaction rate is low. In principle, thick zinc films on platinum and gold will tend towards the same dissolution rate.

A similar situation to that found for the $\mathrm{Zn/H^+/I_2}$ system is observed in the cementation of copper onto zinc, as shown in Fig. 6. Here the measured cementation rate exceeds the sum of the dissolution reaction in acid and the dissolution associated with the displacement of copper from solution. However, it is no longer necessary to suppose that the substrate electrode is promoting the corrosion of zinc since it is known that copper cemented onto zinc can accelerate its dissolution in acid [14]. This is because the standard exchange current density for hydrogen evolution on copper in acidic solutions is appreciably larger than that for zinc [13].

Using the results presented above as examples, it is now possible to examine the validity of previous studies which have used the chronopotentiometric method. The first of these papers is that of Barth *et al.* [1] in which the technique was originally

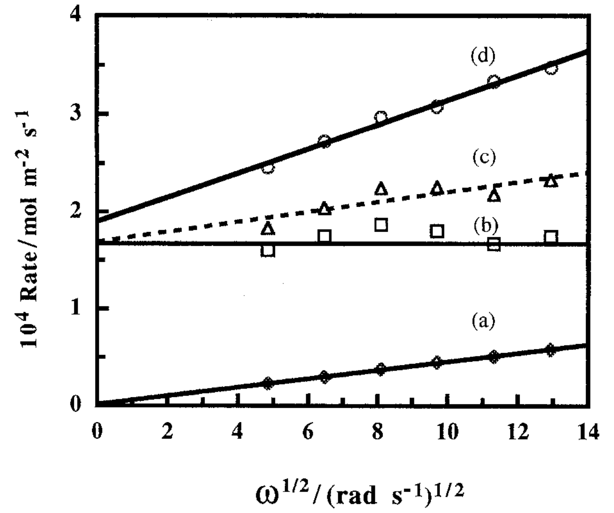

Fig. 6. Cementation of Cu(II) by Zn from gold substrate electrode in solutions. Curves (a) 1.0×10^{-3} M $CuSO_4$, 0.50 M Na_2SO_4, pH 4.0; (b) 0.045 M H_2SO_4, 0.50 M Na_2SO_4; (c) curve (a) + curve (b); (d) 1.0×10^{-3} M $CuSO_4$, 0.045 M H_2SO_4, 0.50 M Na_2SO_4.

described. Results from several different dissolution and cementation reactions are given. Unfortunately, it is difficult to comment on these results since the pH's of the solutions used are not given. On the other hand, it is possible to make a judgement on the results of other studies in which the chronopotentiometric method has been used.

Couche and Ritchie [2] investigated the dissolution of copper films deposited on a gold disc electrode rotating in acidified acetonitrile/water mixtures containing iron (III). These authors found that the dissolution reaction was diffusion controlled. It is therefore similar to the dissolution of zinc films in triiodide solutions, described above. There is no effect of the substrate electrode and the results are correct.

Schalch and Nicol [3] examined the cementation of copper on an iron film which had been plated on a rotating platinum electrode. In this case, the results could be in error since the overpotential for hydrogen evolution on copper is less than that on iron [13]. Consequently, the presence of the copper deposit could promote the corrosion of iron, as it does the corrosion of zinc [14]. However, in the case of Schalch and Nicol's work [3], the effect of the copper deposit on the iron dissolution rate is probably rather small. The reason for this is that they used sodium sulphate as a background electrolyte. Although the pH was not specified, the solution would have been alkaline and the hydrogen ion concentration very low. Thus iron dissolution would have been due only to the cementation reaction which was diffusion controlled. One can, therefore have confidence in these results.

Jiang Xiong and Ritchie [4] used the chronopotentiometric method to investigate the cementation of copper (II) by zinc in a solution at pH 5.7. This is similar to the system investigated in this paper but the pH is much higher. Unlike the results obtained in the present study (see Fig. 6), Jiang Xiong and Ritchie found that the overall zinc dissolution rate was comparable to other measurements of the same quantity and, within the limits of experimental error, was equal to the sum of the rates of the two component reactions; one due to the reaction with copper (II) and the other due to the reaction with hydrogen ions. The difference between the two sets of measurements is undoubtedly due to the difference in pH. In the present study, the dissolution of zinc by acid was more important than the cementation reaction; in the previous study of Jiang Xiong and Ritchie, the reverse was true.

We will consider next the work of Barin *et al.* [5] who studied the cementation of gold by zinc in alkaline cyanide solutions. These authors measured the rate of dissolution of zinc using the chronopotentiometric method both during the cementation reaction and during the dissolution of zinc in alkaline cyanide solutions in the absence of gold. They then *assumed* that the difference between these two dissolution rates was equal to the rate of the cementation reaction by itself. From the foregoing copper (II)/zinc example, it is clear that this subtraction process is only valid if gold does not catalyse the dissolution of zinc. The validity of this assumption will now be considered.

As before, the zinc dissolution reaction is made up of two half reactions: the oxidation of zinc in alkaline cyanide solutions which we will assume here, for the sake of simplicity, gives the tetracyanozincate (II) species

$$\mathrm{Zn} + 4\mathrm{CN}^- \longrightarrow \mathrm{Zn(CN)}_4^{2-} + 2\mathrm{e}^- \qquad (7)$$

and the reduction of water

$$2\mathrm{H_2O} + 2\mathrm{e}^- \longrightarrow \mathrm{H_2} + 2\mathrm{OH}^- \qquad (8)$$

Thus if the reduction of water to hydrogen, according to Equation 8, is faster on a gold surface than on a zinc surface, the gold deposit from the cementation will catalyse the dissolution of the zinc film.

Unfortunately, the review of the hydrogen evolution reaction in alkaline solutions by Appleby *et al.* [13] does not give sufficient data about the standard exchange current densities on gold and zinc to be able to answer this question unequivocally. In addition, it might be argued that such information need not necessarily apply to alkaline solutions containing cyanide ions. The question must therefore be resolved experimentally. Ideally, it would be desirable to undertake additional experiments, similar to those described earlier for the cementation by zinc of copper (II) in acidic solutions, but for the cementation by zinc of gold (I) in alkaline cyanide solutions. Unfortunately, this cannot be achieved as easily as it was in the case of the copper (II)/zinc system. This is because lowering the pH to minimize the reaction between zinc metal and water would cause the formation of hydrocyanic acid.

To overcome this difficulty, two additional experiments were performed. In the first, a gold wire (1.0 mm dia.) was inserted in a tight fitting hole drilled in a block of zinc (a rough cube of about 1 cm side). This couple was then placed in a solution containing 1×10^{-2} M cyanide and 1×10^{-2} M sodium hydroxide. Almost immediately, reaction occurred;

the zinc block was etched and the microcrystals in its structure became visible. Hydrogen bubbles were evolved but *only* on the gold wire, thus confirming that gold catalyses the dissolution of zinc in alkaline cyanide solutions. In the second set of experiments, a gold ring, gold disc electrode rotating at 200 rpm was used. The gold disc was plated with a zinc film using a plating current of 0.050 mA for 100 s. The time taken for it to dissolve at 25 °C in an alkaline cyanide solution containing 1.0×10^{-2} M cyanide and 1×10^{-2} M sodium hydroxide was measured by chronopotentiometry (see Fig. 1). When the disc electrode was not connected to the ring electrode, the dissolution time was 545 ± 20 s. However, when the disc electrode was electrically connected to the gold ring electrode, the dissolution time fell to 145 ± 15 s (i.e., a rate increase of nearly four times). It should be noted that it was necessary to replace the reaction solution after each run to maintain the quality of the chronopotentiograms. It is believed that this problem is due to the build up of zinc in solution. The above results are incontrovertible proof that gold catalyses the dissolution of zinc in alkaline cyanide solutions. From these results, it is clear that Barin *et al.* [5] were not justified in their subtraction process and so their calculated values for the cementation by zinc of gold in alkaline cyanide solutions must be incorrect.

4. Conclusions

The results show that, in chronopotentiometric studies of metal dissolution and cementation reactions, the substrate has no influence on the rate if the reaction is diffusion controlled. However, it markedly affects the rate of chemically controlled reactions. The magnitude of the effect is related to the catalytic activity of the inert substrate. Furthermore, widening of the holes in the layer of the metal undergoing dissolution enhances the exposure of the catalysing inert substrate surface leading to an increased reaction rate. Thus the measured rate with a reaction mixture sometimes exceeds the sum of the two component reactions proceeding independently. The same applies to those cementation reactions which proceed concurrently with a chemically controlled dissolution reaction, such as proton reduction, which is catalysed by the precipitated metal. For example, in the cementation of copper on zinc in acid solutions, the rate of the cementation reaction cannot be measured by measuring the rate of cementation in acid and without acid, and then subtracting one from the other. In the light of this knowledge, the validity of other rate studies, which have been carried out using the chronopotentiometric method and which have been reported in the literature have been reviewed. It was concluded that the method used by Barin *et al.* [5] to determine the rate of cementation of gold by zinc from alkaline cyanide solutions needs reevaluation. Their method neglects the catalytic effect of the precipitated gold on the rate of zinc dissolution in alkaline cyanide solution.

Acknowledgements

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