

A capacitance study of the silver(I)/copper displacement reaction

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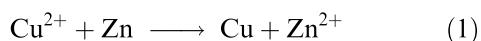
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Received 11 March 1996; revised 9 May 1996

Metal displacement (cementation) reactions are usually diffusion controlled and conform to first order kinetics. When a displacement reaction is carried out in a batch reactor, positive deviations from a first order rate plot are commonly observed once the deposit becomes sufficiently thick. It has been suggested that these rate enhancements are the result of changes in deposit structure resulting in increases in surface area. Another theory argues that the rate enhancements are due to turbulence associated with increasing roughness of the deposit. In this paper, an attempt is made to discriminate between these two possibilities by measuring the capacitance of a copper electrode immersed in a silver(I) solution. It was found that no anomalous capacitance changes were observed corresponding to the region in which rate increases were observed. This suggests that turbulence effects, rather than area effects, are responsible for the increased reaction rate. Capacitance measurements were also conducted for the reaction between silver(I) and copper in the presence of cyanide which caused the silver to deposit in a thin uniform layer on the copper surface, thus blocking the displacement reaction. It was found that the capacitance changed very little with time under these circumstances.

1. Introduction

Metal displacement reactions (or, as they are more commonly known in the mining industry, cementation reactions) are reactions in which a more noble metal is displaced from solution by a less noble metal. An example of such a reaction, which is used in the electrolytic process for zinc [1], is the displacement of copper from solution by zinc powder, the relevant equation being



A metal displacement reaction is a type of corrosion reaction in which the anodic half-reaction is the dissolution of the less noble metal and the cathodic half-reaction is the deposition of the more noble metal. Cementation reactions can therefore be investigated using many of the electrochemical methods developed to study corrosion reactions [2].

By far the largest number of metal displacement reactions investigated to date are controlled by the rate of diffusion of the more noble metal ions to the reacting surface [2]. Only a small number have been shown to be chemically controlled and this type of reaction will not be considered further here. The kinetics of a diffusion controlled cementation reaction taking place in a reaction vessel of constant volume should conform to a first order rate law of which the integrated form is [2]

$$\ln\left(\frac{C_0}{C}\right) = \frac{kAt}{V} \quad (2)$$

where C_0 is the initial concentration of the more noble metal ions in solution, C is the concentration after time t , k is the rate constant and A the area of the less noble metal. In the case when the less noble metal is in the form of a disc rotating at speed ω , the rate constant k is given by [2]

$$k = 0.62 D^{2/3} \nu^{-1/6} \omega^{1/2} \quad (3)$$

where D is the diffusion coefficient of the more noble metal ions and ν is the kinematic viscosity of the reactant solution.

The kinetics of most cementation reactions investigated to date, using a sample of the less noble metal in the form of a rotating disc, conform to Equations 2 and 3 provided the deposit thickness is not too great [3]. Thus, these equations obtain when the concentration of the more noble metal is low (say, less than 10^{-4} M) or, if the concentration is high, only in the initial stages of the reaction. Above some critical thickness, the rate increases sharply. Two causes for this rate enhancement have been proposed. According to the first of these proposals [4, 5], rate increases could occur as a result of increases in the cathodic area. However, such an argument is not likely to apply to a rotating disc system where only the geometric area is important [6]. Strickland and Lawson [3] have therefore proposed that the observed increase in rate is due to turbulence at the disc surface as a result of the surface roughening associated with deposit growth. Although this is an entirely reasonable hypothesis, there is little direct evidence to support it.

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This paper describes some measurements of the capacitance of a reacting surface during a cementation reaction, together with the kinetics of that reaction. In a system at equilibrium, the capacitance is proportional to the surface area and so provides a convenient means of monitoring this latter quantity. In a reacting system, contributions to the total capacitance can arise from the reaction itself [7]. However, provided the contributions to the capacitance from the reaction are not large, changes in surface area will still be reflected by changes in capacitance. Thus, capacitance measurements can, under appropriate conditions, be used to determine whether the rapid increase in reaction rate observed in many cementation reactions is associated with a corresponding sharp increase in surface area of the deposit.

In addition to positive deviations from a first order kinetic plot, negative deviations are known to occur when the deposit blankets the substrate, blocking the cementation reaction. Such reactions have considerable importance in metal finishing. For example, Lechtman [8] has demonstrated that pre-Columbian Indians in South America almost certainly made gold plated copper objects by cementation using conditions under which the gold was deposited on nearly all of the copper surface. More recently, Robertson *et al.* [9] have shown that thin blocking films of zinc on aluminium are deposited from an alkaline zincate solution when the zincate concentration is high and when the rate of stirring is rapid. Capacitance measurements recorded for a blocking reaction are also described in this paper.

2. Experimental details

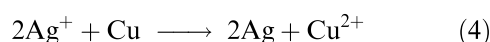
All solutions were prepared using deionized water obtained from a Millipore Milli-Q system. The reagents used were of analytical grade with the exception of silver cyanide and sodium cyanide, which had minimum assays of 99% and 97.0%, respectively. All solutions were deaerated with high purity nitrogen before the experiment commenced, and a nitrogen atmosphere was maintained for the duration of the experiment. 250 mL of test solution was used and a thermostated water bath maintained the temperature at $25.0 \pm 0.5^\circ\text{C}$. At timed intervals, 1.5 mL samples were removed and analyzed by atomic absorption spectrophotometry. The volume change due to sampling was insufficient to affect the kinetic measurements significantly.

Rotating discs of large surface area ($A_{\text{Cu}} = 6.90\text{ cm}^2$, $A_{\text{Zn}} = 7.07\text{ cm}^2$) were pretreated by polishing on various grades of silicon carbide paper up to P4000 and rinsing with deionized water. The rotating disc equipment and cell set up were as described previously [10]. A saturated calomel electrode (SCE) was used as the reference electrode and all potentials reported in this paper are expressed with respect to this. The capacitance measurements were performed using the instrument described by Power and Caldwell [11]. The steady state mixed potential of the reaction

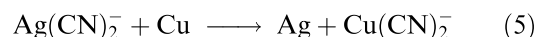
was measured and a PAR (model 173) potentiostat used to impose this potential on the electrode. The output of the capacitance meter, which is a triangular voltage with an amplitude of about 20 mV, was fed to the input of the potentiostat. This produced a current-time response in the form of a square wave at the potentiostat output. This signal was then fed to the input of the capacitance meter, which produced a final output voltage which was proportional to the capacitance of the system.

3. Results and discussion

The silver(I)/copper system was selected for study because there are no complicating side reactions which cause excessive consumption of the less noble metal. Two reactions were investigated. The first was the cementation by copper of silver(I) in a nitric acid solution



for which $E_{298}^\circ = 0.459\text{ V}$ [12]. This reaction results in a nonblocking deposit of silver which, when sufficiently thick, causes the reaction rate to increase. Thus, by changing the silver(I) concentration, it is possible to investigate the reaction without and with rate enhancement. The second reaction is the cementation by copper of silver(I) in an alkaline cyanide solution



for which $E_{298}^\circ = 0.15\text{ V}$ [12]. At appropriate concentrations, the presence of the cyanide ion has the effect of causing surface blocking [13], presumably by increasing the rate of nucleation and lateral growth of the silver deposit on the copper surface.

3.1. Rate unaltered by deposit

In dilute solutions of silver(I) (e.g., 5 ppm or $4.6 \times 10^{-5}\text{ M}$), the deposit does not grow sufficiently thick to interfere with the kinetics of the reaction. As can be seen from the lower set of data points in Fig. 1, the data are a good fit to a first order rate plot over the 80 min of the experiment. Furthermore, there is good agreement between the measured values of $\ln(C_0/C)$ as a function of time and those calculated from Equations 2 and 3 using the experimental parameters A , V and ω and literature values for D and ν . The diffusion coefficient for silver ions was taken to be $1.648 \times 10^{-9}\text{ m}^2\text{ s}^{-1}$ [14], while the kinematic viscosity was interpolated from the data in the CRC *Handbook of Chemistry and Physics* [15] for nitric acid solutions. A value of $1.00 \times 10^{-6}\text{ m}^2\text{ s}^{-1}$ was obtained. Since the kinematic viscosity only enters Equation 3 as the minus one sixth power, the exact value is not critical. Substituting these quantities into Equations 2 and 3 yielded the lower solid line shown in Fig. 1. It can be seen that there is good agreement between this line and the experimental data points.

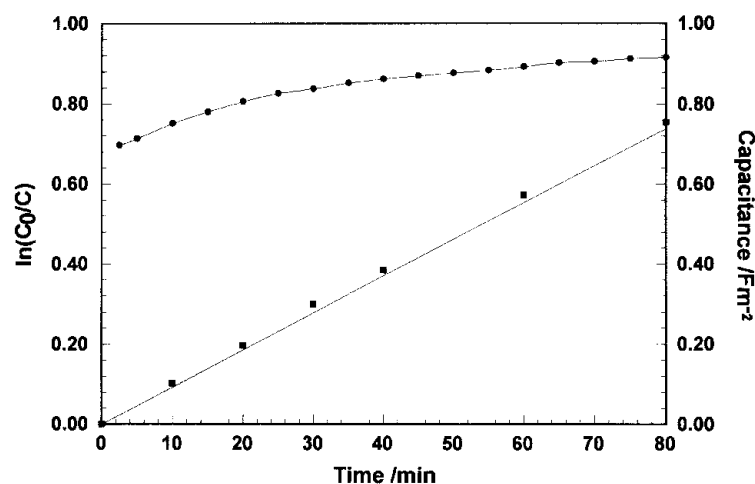


Fig. 1. First order kinetic plot (■) and capacitance measurements (●) as a function of time for the displacement reaction between a solution containing 5 ppm silver(I) in 0.1 M nitric acid and a copper electrode rotating at 400 rpm. The lower solid line was calculated using Equations 2 and 3 and the data presented in the text.

The upper curve in Fig. 1 presents the capacitance measurements recorded as a function of time. The results show that the capacitance increased with time, initially quite quickly before reaching a plateau towards the end of the experiment. This trend is as expected since the depositing silver would undoubtedly be rougher than the original, polished copper surface. Consequently the surface area, and thus the capacitance, of the electrode increases. Eventually, the deposit reached a limiting roughness. Similar results were obtained for the leaching of copper metal in an iron(III) chloride solution.

The magnitude of the capacitance shown in Fig. 1 ($0.7\text{--}0.9\text{ F m}^{-2}$) recorded during the reaction is comparable to that measured without reaction. When the copper electrode was immersed in a solution containing 20 ppm copper ($3.1 \times 10^{-4}\text{ M}$) and 0.1 M sodium sulfate, the capacitance was determined to be about 0.7 F m^{-2} , although this value decreased after approximately 7 min of immersion.

3.2. Rate enhanced by deposit

Figure 2 presents the corresponding curves to those

shown in Fig. 1 for a silver(I) concentration of 20 ppm ($1.9 \times 10^{-4}\text{ M}$). The lower solid line again represents the rate calculated from Equations 2 and 3. It can be seen that the experimental data points for the first 20 to 25 min of the reaction are in close agreement with the predicted values. However, after this time, the rate increases rapidly as indicated by the dotted line. The upper curve in Fig. 2, which shows the plot of capacitance against time, clearly demonstrates that the sharp increase in reaction rate is not associated with a corresponding sharp increase in capacitance. Rather, the change in capacitance with time is similar to that observed for 5 ppm silver(I), that is, the capacitance initially increased quite rapidly with time before tending towards a limiting value by the end of the experiment. Not surprisingly, the total increase in capacitance was much greater for 20 ppm silver(I) than 5 ppm. This is because the faster deposition rate, which occurred at the higher concentration of silver, leads to the formation of rougher silver deposits on the copper surface. It may be concluded that changes in the surface area of the deposit *per se* do not lead to the sharp increase in the kinetic plots. This result therefore leaves the turbulence theory of

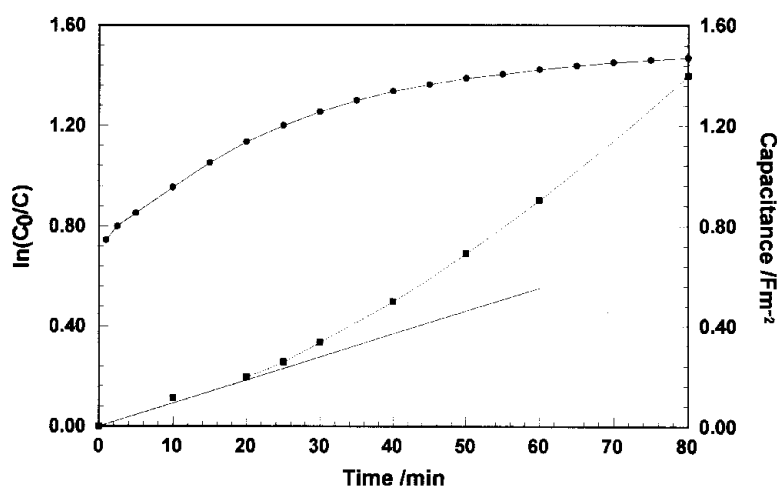


Fig. 2. First order kinetic plot (■) and capacitance measurements (●) as a function of time for the displacement reaction between a solution containing 20 ppm silver(I) in 0.1 M nitric acid and a copper electrode rotating at 400 rpm. The lower solid line was calculated using Equations 2 and 3 and the data presented in the text.

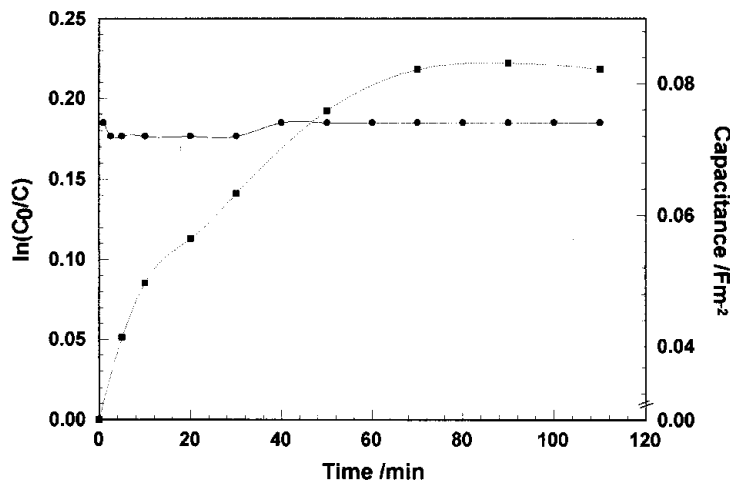


Fig. 3. First order kinetic plot (■) and capacitance measurements (●) as a function of time for the displacement reaction between a solution containing 5 ppm silver(I), as silver cyanide, in 2.50×10^{-4} M sodium cyanide, 0.1 M sodium hydroxide and a copper electrode rotating at 400 rpm.

Strickland and Lawson [3] as the most likely explanation for the sharp increase in reaction rate when the deposit reaches some critical thickness.

3.3. Rate retarded by deposit

The cementation of silver by copper from an alkaline cyanide solution is known to produce a blocking deposit [13]. Figure 3 shows the first order kinetic plot for the conditions of 4.6×10^{-5} M silver cyanide (5 ppm silver), 2.5×10^{-4} M sodium cyanide and 0.1 M sodium hydroxide. It can be seen that after 60 min, the cementation rate of silver slowed and then stopped completely. Consistent with this, the deposit was found to be very smooth, coherent and adherent. The corresponding capacitance measurements also presented in Fig. 3, show that the surface area of the electrode changed little with time, even in the first 60 minutes of the reaction when the substrate was not blocked. This indicates that the silver deposit laid down in that period was compact, and occupied approximately the same area as the copper it covered.

Figure 4 shows the mixed potential for the displacement of silver by copper from an alkaline cyanide

solution. As can be seen, the mixed potential initially fell before rising slowly to a value characteristic of silver metal in a solution of the same composition. It is clear that, at this point, the copper surface was essentially covered by the silver deposit. For the copper surface to be coated in this way, rapid nucleation and lateral growth of the silver must have dominated the deposition process.

4. Conclusions

The following conclusions can now be made:

- (i) In dilute silver(I) solutions, i.e. 5 ppm, the cementation rate is unaffected by the presence of a deposit on the copper disc. The capacitance was found to increase quite quickly at the start of the reaction, undoubtedly as a result of the roughness of the silver deposit relative to the original, polished copper surface. Towards the end of the experiment the capacitance was found to reach a plateau, indicating that the deposit had attained a limiting roughness.
- (ii) At the higher concentration of silver(I) (i.e., 20 ppm) the total change in capacitance was greater

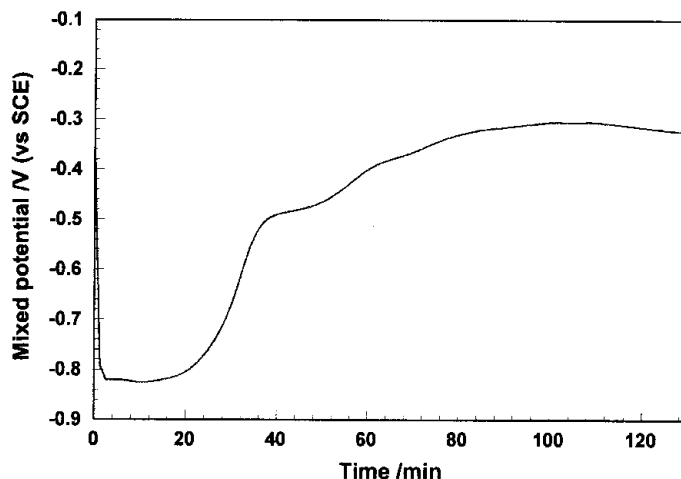


Fig. 4. Mixed potential as a function of time for a copper electrode rotating at 400 rpm immersed in a solution containing 5 ppm silver(I), as silver cyanide, 2.50×10^{-4} M sodium cyanide and 0.1 M sodium hydroxide.

than that measured in the dilute silver(I) solution. A sharp increase in the rate of cementation was observed after 20 to 25 min reaction time, which was not associated with any rapid increase in the capacitance measurements. Thus changes in the surface area of the cementation deposit do not lead to an enhancement in the rate of deposition. This suggests that turbulence is the most likely cause of the increased reaction rate.

(iii) The blocking deposit formed in the alkaline cyanide solution was adherent and coherent, with rapid nucleation and lateral growth being the dominant deposition processes. In the period prior to blocking of the substrate, no significant change in the capacitance was measured, indicating that the silver deposit laid down occupied approximately the same area as the copper it covered.

Acknowledgements

The authors are grateful to the Cooperative Research Centre Programme of the Australian Government which has supported this work.

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