Reverse pulse plating of copper from acid electrolyte: a rotating ring disc electrode study

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Coulombic or cathode efficiencies (CE) were determined for the reverse pulse plating of copper from $CuSO_4/H_2SO_4$ electrolyte for a variety of pulse conditions. The CE was seen to decrease as the magnitude of the current on the anodic pulse increased. This may be explained by an increase in Cu^+ intermediates near the electrode surface and was verified by polarization data obtained from a rotating ring disc electrode (RRDE). The influence of certain additives on the CE during reverse pulse plating and on the polarization curves was also examined. When polyethylene glycol and Cl^- (0.86 mM) were added to the electrolyte, the CE was observed to drop significantly for a particular set of pulse parameters. The polarization curves at the RRDE suggested that the copper–electrolyte interface was blocked by an adsorbed layer over a wide potential range. The results are explained in terms of a model in which Cl^- ions are concentrated near the electrode surface within the adsorbed polyethylene glycol layer and this is supported by observed rotational dependencies for the RRDE.

1. Introduction

There have been a number of studies which address the use of pulse plating (PP) techniques for copper metal deposition. A review of existing literature has been presented by Wan et al. [1]. Some of the advantages cited for the application of PP techniques include an increase in the overall plating rate [2] and finer grain structure [3–6] with improved mechanical properties [7]. There has been some evidence that throwing power may be enhanced under certain conditions, but this appears to remain controversial for copper deposition [8]. There have been fewer studies conducted with reverse pulse plating (RPP), although a number of parameters were examined for deposition of copper from an acid electrolyte using RPP [9].

The basic electrochemistry for copper deposition and dissolution from acid electrolyte was elucidated by the application of galvanostatic techniques [10]. The deposition of Cu^{2+} was determined to occur via a two-step mechanism, according to the following equations:

$$Cu^{2+} + e \longrightarrow Cu^+ \qquad (1)$$

$$Cu^+ + e \longrightarrow Cu \qquad (2)$$
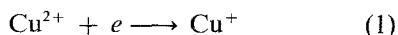
For d.c. plating at high overpotentials, reaction 1 constitutes the kinetically limiting process. Thus, reaction 2 is in equilibrium with the copper surface and the Cu^+ concentration near the electrode surface is small. Further, the cathode efficiency (CE) for the copper deposition with d.c. plating is very near 100%. These equilibria were used to explain an observed loss in CE for the deposition of copper under PP conditions [11]. For this case, the concentration of Cu^+ near the electrode surface increases since the electrode potential has excursions into a regime where Cu^+ is stable (e.g. it is not reduced by electron transfer from the electrode surface, although it may disproportionate). Thus, the concentration of Cu^+ near the electrode surface increases and may be lost to the bulk solution, by convection or diffusion, resulting in a loss of coulombic efficiency. The use of a rotating ring disc electrode (RRDE) may be employed to confirm the presence of stabilized Cu^+ [12, 13]. As Cu^+ is swept away from the vicinity of the disc surface it may be detected at the ring electrode, assuming the ring potential is maintained

in the limiting current region for the oxidation of Cu^+ to Cu^{2+}.

In the present study, the CE for copper deposition under RPP conditions are studied. The observed CE for various conditions are explained by the polarization behaviour observed at a RRDE for both the metal deposition and dissolution. Also included are the effects of certain additives on the CE and polarization behaviour. The presence of polyethylene glycol (PEG) together with Cl^- have been shown to polarize the copper–electrolyte interface for both copper deposition and dissolution [14]. We have examined the effects of the absorption of polyethylene glycol (PEG) and Cl^- on the CE under RPP conditions and, again, explained the behaviour with data from a RRDE.

2. Experimental details

Polarization experiments were performed in a standard three-compartment electrochemical cell (100 ml volume) fitted with a Luggin capillary. The working electrode was a platinum disc (area $0.16 \, cm^2$) platinum ring (area $0.037 \, cm^2$) RRDE (Pine Instruments, Model AFMT28PTPT) employing a Pine Inst. rotator (Model AFMSR). The electrode was polished with successively finer grades of alumina, the final polish being with $0.05 \, \mu m$ gamma alumina, followed by a distilled water rinse. The counter electrode was platinum foil (area $8 \, cm^2$) and the reference was a saturated calomel electrode (SCE). Polyethylene glycol was purchased from Fisher Sci. as carbowax PEG 20M (average mol wt 20 000) and carbowax PEG 3350 (average mol wt 3350). All other chemicals were reagent grade and used without further purification. All solutions were prepared with deionized water and were deaerated with argon prior to the measurements. A Pine Inst. potentiostat (model AFRDE4) and a Yokogawa two-pen x–y recorder were used to obtain polarization data.

Pulse plating experiments and cathode efficiencies were determined with a Princeton Applied Research (PAR) model 173 potentiostat–galvanostat fitted with a PAR Model 179 digital coulometer and a PAR Model 175 Universal Programmer. Electrochemical transients

were recorded with a Nicolet digital oscilloscope (Model 2094). Efficiencies were determined by monitoring the number of coulombs passed during the pulsed experiments, which was nominally 1.0 C. The electrode, with the plated copper film, was then transferred to a second electrochemical cell containing $1.0 \, M \, H_2SO_4$. The copper film was stripped anodically and the number of coulombs was recorded. The efficiency was defined as the number of coulombs during the pulsed experiment divided by the number of coulombs during the anodic stripping.

The RPP experiments were performed with a cathodic current pulse (i_c) of $17.0 \, mA$ ($50 \, mA \, cm^{-2}$). The current on the anodic pulse (i_a) was variable and the values selected were 0, 4.25, 8.5, and 17.25 mA. These correspond to 0, 25, 50 and 75% of i_c. Therefore, the average current density for plating decreased as i_a increased. The pulse time for i_c and i_a was always equivalent, although values of 1.0, 10 and 100 ms were studied.

3. Results and discussion

The polarization curves for an RRDE in 0.31 M $CuSO_4$ are shown in Fig. 1. The platinum disc electrode had an electrodeposited copper film approximately $1 \, \mu m$ thick. The potential was poised at the Cu/Cu^{2+} rest potential (54 mV vs SCE) and then stepped incrementally, first in the cathodic direction, followed by a return to the rest potential, then in the anodic direction. For the cathodic branch, at low overpotentials (eg. $< -100 \, mV$) small quantities of Cu^+ were produced, as indicated by the observed ring current. This observation is in agreement with previous reports and explains the loss of CE for pulse plating [12]. However, for cathodic overpotentials more negative than $-100 \, mV$, the ring current decayed to a background level indicating that cuprous production at the disc had ceased. For the anodic branch, the ring current was seen to increase continually, although the rate of increase was less for overpotentials more positive than 100 mV.

The polarization behaviour at the RRDE is useful for explaining the CE values obtained for the RPP of copper from the same electrolyte. The reduction of the CE for PP has previously
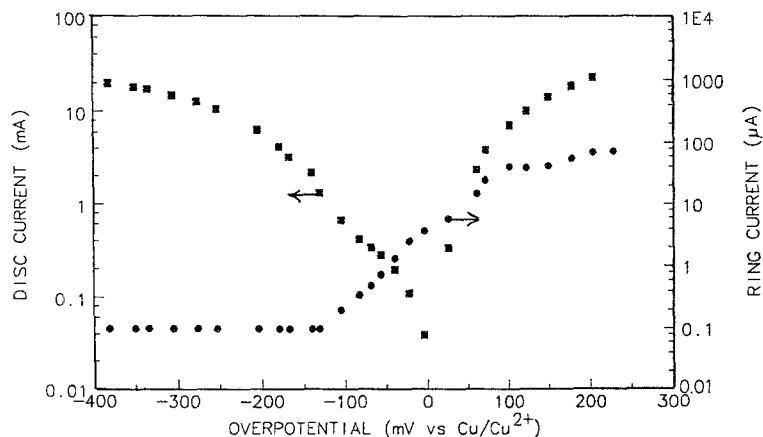
Fig. 1. Current versus overpotential curves at an RRDE for a solution composed of 0.31 M $CuSO_4$ and 1.0 M H_2SO_4. The rotation rate was 900 rpm. The ring electrode was maintained at 0.4 V vs SCE. The disc was allowed to reach equilibrium at each potential prior to making measurements.

been attributed to stabilization of Cu^+ near the cathode surface which is subsequently lost to the bulk solution by mass transfer [11, 12]. The situation for RPP is analogous. As the reverse current is increased in magnitude the CE was observed to decrease (Fig. 2). This is attributable to increasing quantities of Cu^+ produced as the magnitude of the anodic current, applied during the reverse pulse, increased and is verified by the increasing ring currents observed during anodic polarizations.

CE data was obtained at three pulsing frequencies. For PP ($i_a = 0$) the CE was observed to decrease in the order 10 > 100 > 1000 Hz, in agreement with previously reported results [11], although the differences were small. However, as reverse pulsing commenced, the order reversed. This may be explained by observation of the transient potential response to the square wave current signal (Fig. 3). A typical transient for RPP ($i_a = 0.25 i_c$) at a pulse of 10.0 ms is

shown in curve A. For the anodic pulse, the potential approached the steady state value corresponding to an anodic current of 4.25 mA. In contrast, the analogous transient at a pulse of 1.0 ms shows that the electrode was not able to obtain the same positive potential. In fact, during the anodic pulse, the electrode potential was only slightly more positive than the rest potential. The effective lag in potential was not seen to be as severe during the cathodic pulse. Since Cu^+ is generated in larger quantities at more positive potentials, it follows that the slower pulse frequencies would have lower efficiencies.

The addition of PEG 3350 to the electrolyte had little influence on the CE for RPP, compared to the response in the absence of PEG, except when $i_a = 0.75 i_c$ (Fig. 4A). However, addition of 0.86 mM Cl^- and PEG 3350 resulted in a significant reduction in CE for all values of i_a (Fig. 4B). This may, again, be explained by
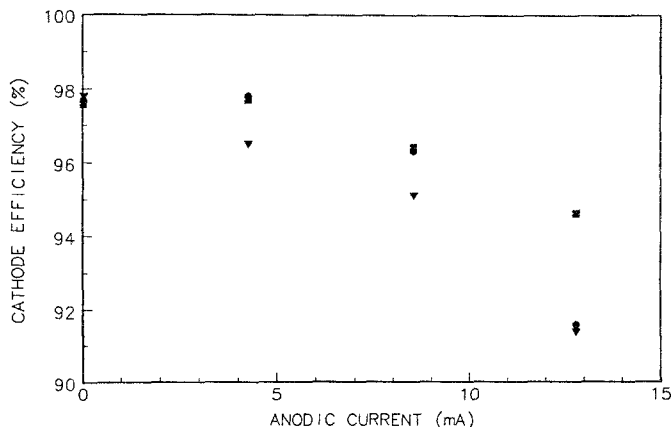

Fig. 2. Cathode efficiency versus magnitude of the current for the anodic pulse. i_a is 0, 4.25, 8.5 and 12.75 mA and i_c is 17.0 mA. The pulse duration was 1.0 (■), 10 (●) and 100 (▼) ms/pulse.
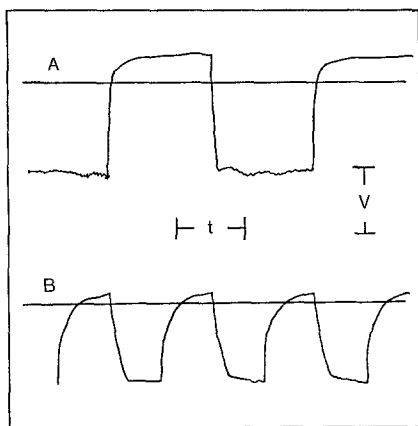
Fig. 3. Overpotential versus time curves for a RRDE in the same solution as Fig. 1. The pulse times are 10 and 1.0 ms for curves A and B, respectively. The horizontal line through each curves denotes the open circuit rest potential of 54 mV vs SCE. Positive potentials are up. For the potential axis, $V = 160$ mV and for the time axis, $t = 6.66$ and 1.33 ms for curves A and B, respectively.

observed polarization behaviour at the RRDE (Fig. 5). The qualitative features of the cathodic branch are the same as those observed in the absence of PEG and Cl⁻ with regard to the production of Cu⁺ at the disc. However, the disc currents are much lower in the presence of the additives, attributable to a more polarized interface [14]. PEG alone or 0.86 mM Cl⁻ alone only slightly affected the polarization behaviour (not shown), but the two in combination had a dramatic influence.

The interface remained polarized on the anodic branch in the presence of PEG and Cl⁻ (Fig. 5), as reflected by the lower observed disc currents. The ring currents were substantially higher than those obtained in the absence of

additives indicating enhanced stabilization of Cu⁺ at the cathode interface. This observation explains the decrease in the CE observed for RRP in the presence of PEG and Cl⁻. Increasing the molecular weight of the PEG from 3350 to 20 000 further decreased the CE at each value of i_a (Fig. 4C).

An explanation has been offered for the observed polarization of the copper–electrolyte interface in the presence of PEG and Cl⁻ [14]. Cu⁺ may be complexed by PEG molecules, resulting in a polymer matrix with a net positive charge. The polymer complex is then attracted to Cl⁻ ions which are adsorbed on the copper surface, resulting in the Cl⁻-induced adsorption of the PEG–Cu⁺ complex, which effectively polarizes the surface.

This may indeed be the mechanism of PEG adsorption at the copper surface but it does not completely account for the loss of CE observed in the RPP experiments. The scheme shown in Fig. 6 would more completely account for the observed reduction in CE in the presence of PEG and Cl⁻. It is clear from the polarization data that there is an adsorbed layer blocking the electrode surface over the entire potential range studied. There is Cl⁻ present both in the bulk of solution and within the adsorbed layer of film of PEG. A partition coefficient, K_D, for the extraction of Cl⁻ from solution and into the film, may be defined by Equation 3:

$$K_D = Cl^-_{film}/Cl^-_{soln} > 1 \qquad (3)$$

The result is locally high concentrations of Cl⁻ within the adsorbed PEG layer. The mechanism of Cl⁻ concentration into the film may be
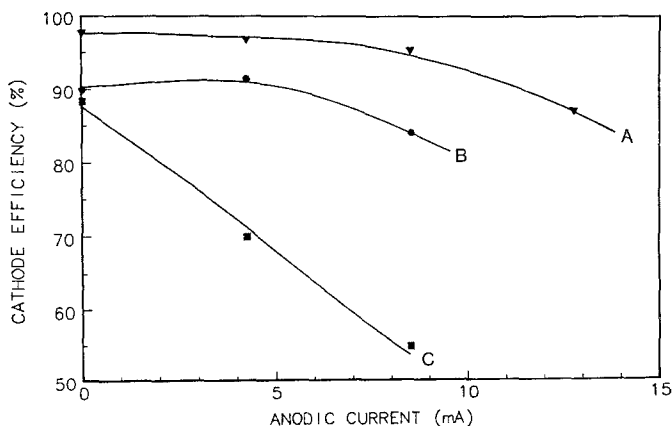

Fig. 4. Cathode efficiency versus magnitude of current on anodic pulse. The pulse parameters are identical to those in Fig. 2. The solution composition was also the same except for the addition of 0.1% PEG 3350 (▼), 0.1% PEG 3350 and 0.86 mM NaCl (●) and 0.1% PEG 20 000 and 0.86 mM NaCl (■).
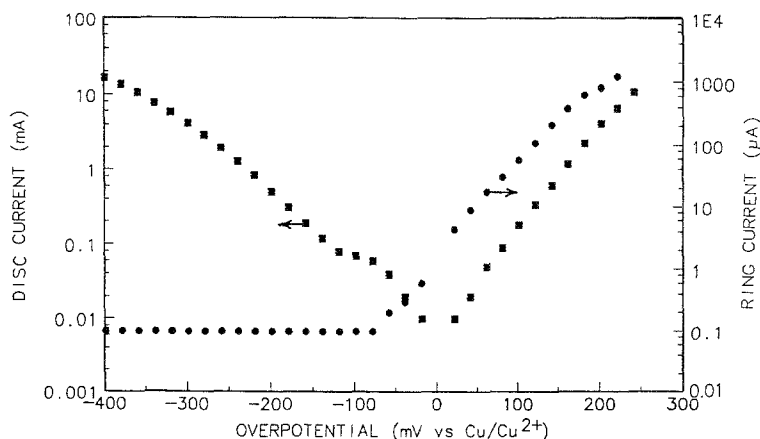
Fig. 5. Current vs overpotential curves for an RRDE in 0.31 M $CuSO_4$, 1.0 M H_2SO_4, 0.1% PEG 3350 and 0.86 M NaCl. The electrode rotation rate was 900 r.p.m.

attributed to electrostatic attraction of Cl^- to PEG–Cu^+ complexes or to the protonation of PEG at this pH which would result in a positively charged matrix. We have not verified the latter, but it appears plausible.

There is experimental evidence to support this model. First, when the RPP experiments were performed in the presence of higher Cl^- concentrations (e.g. 50 mM Cl^-) and in the absence of PEG (Fig. 7), the CE were very similar to those observed for PEG with 0.86 mM Cl^-. Thus, the latter appears to have the effect of increasing the Cl^- concentration near the electrode surface. This effect cannot be attributed solely to complexation and stabilization of Cu^+ by PEG since there would be no mechanism by which Cu^+ could escape the film. The observation of significant ring currents during steady-state polarizations, eliminates this possibility.
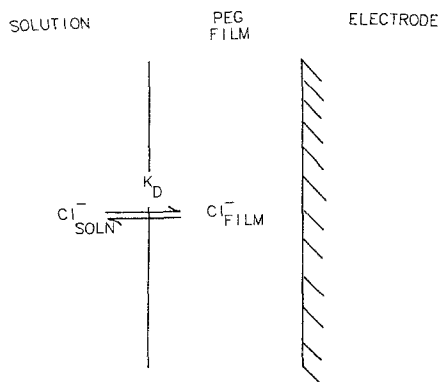

Fig. 6. Schematic representation of an electrode surface modified with an adsorbed layer of PEG. The equilibrium is shown between the Cl^- concentration in solution and in the film, with an equilibrium constant K_D.

Further evidence comes from the rotation dependence of the CE (Fig. 8). When the electrode was pulse plated at 100 Hz, the CE was observed to decrease as the rotation rate increased. This is consistent with observations made by Wan et al. [11] and supports the argument that Cu^+ is being swept from the electrode surface by convection arising from rotation. More material is removed at higher rotation rates. However, for the case of the electrode surface with an adsorbed PEG–Cl^- layer, the CE appears to be independent of rotation rate. This may be explained as follows. Cu^+ ions may be stabilized by Cl^- near the electrode surface within the adsorbed PEG layer. There is a net flux of Cu^+ flowing from the film as evidenced by the overall reduction in CE and observed ring currents during steady-state polarizations. However, the absence of a rotation dependence indicates that the equilibria associated with Cl^- stabilization take place within the adsorbed PEG film and, therefore, are not subject to the changes in convection that occur due to changes in the electrode rotation rate. The absence of a rotation dependence for electron transfer processes occurring at electrode surfaces modified by films has been well documented [15–18].

4. Conclusion

The CE efficiency for RPP is lower than that for PP or for d.c. plating. This is explained by the stabilization of Cu^+ near the cathode–electrolyte interface, which becomes more predominate with excursions into the anodic
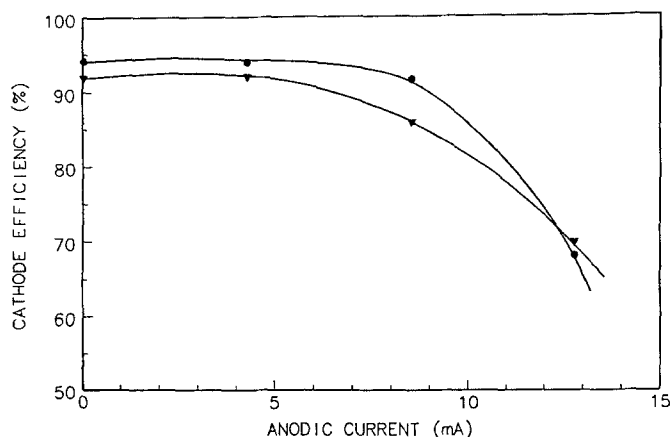
Fig. 7. Cathode efficiency vs the magnitude of the anodic current on the reverse pulse. The pulse parameters and solution composition is the same as in Fig. 2, with the exception of the addition of 50.0 mM NaCl. The pulse times are 100 (▼) and 10 (●) ms/pulse.
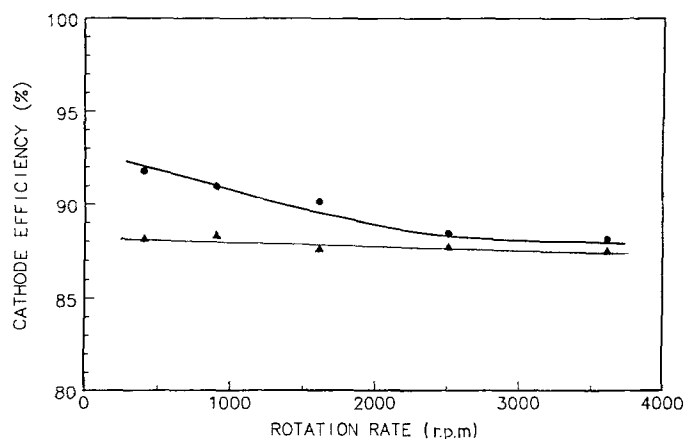

Fig. 8. Cathode efficiency vs electrode rotation rate for a solution of the same composition as in Fig. 2 (●) and with the addition of 0.1% PEG 20 000 and 0.86 mM NaCl (▲).

branch (e.g. copper dissolution). The presence of PEG or Cl^- alone has little influence on the CE when compared to d.c. plating. However, the combination of the two forms an adsorbed layer which effectively polarizes the surface over a large potential range. The result of the adsorbed layer is to produce locally high concentrations of Cl^- near the electrode surface by extracting Cl^- from solution. The result is a loss in cathode efficiency. Current efforts in this area involve a detailed study of the metallurgy derived from RPP in the presence and absence of certain additives.

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