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A study of electrochemical kinetics of copper deposition under pulsed current conditions

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The investigation is concerned with the drop of current efficiency (CE) of copper deposition under pulsed current conditions. A mathematical model which is based on different charge transfer rates between the following two reactions,

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

and

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

has been formulated to describe the behaviour of a $Cu/CuSO_4$ system under pulsed current conditions on a rotating disc electrode. The results indicate that the CE drops continuously as the difference between the exchange current densities of the two reactions increases. The exchange current densities of Reactions 1 and 2 were estimated to be 0·034 mA cm^{-2} and 0·024 mA cm^{-2}, respectively. Prediction of CE using the mathematical model agreed to within 3·5% with experimental data over a range 80·4–93·7%.

List of symbols

C_A, C_B	concentrations of Species A and B
C_A^o, C_B^o	bulk concentration of Species A and B
C_A^s, C_B^s	surface concentration of Species A and B
CE	current efficiency of copper deposition
D_A, D_B	diffusion coefficients of Species A and B
i_1, i_2	partial current densities of Reactions 3 and 4
i_{o_1}, i_{o_2}	exchange current densities of Reactions 3 and 4
I_1, I_2	total currents of Reactions 3 and 4
F	Faraday's constant
k, k'	forward and reversed rate constants of Reaction 5
r	radial coordinate
r_o	radius of rotating disc electrode
R	universal gas constant
t	time
$t_{Cu^{2+}}$	transport number of Cu^{2+}
T	temperature
v_x	velocity of the electrolyte in the axial direction
x	axial coordinate
$\alpha_{c_1}, \alpha_{a_1}$	cathodic and anodic transfer coefficients of Reaction 3
$\alpha_{c_2}, \alpha_{a_2}$	cathodic and anodic transfer coefficients of Reaction 4
δ	diffusion layer thickness (Nernst layer)
η	electrode overpotential
ω	rotation speed

1. Introduction

Current efficiency (CE) of copper plating from acidic copper sulphate baths is generally close to 100% under reasonable d.c. conditions. However it was observed in our laboratory that the current efficiency for copper deposition under pulsed current conditions with a relatively long relaxation time was distinctly below 100% [1, 2]. The CE drops continuously as either the relaxation time is lengthened or the pulse time is shortened. This observation raises considerable doubt as to the reliability of a number of kinetic studies reported in the literature under galvanostatic conditions by assuming a 100% CE for the reaction under study.

In this paper, a theoretical model [3] which is based on different charge transfer rates between the two following reactions

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

and

$$\mathrm{Cu^{+} + e \rightarrow Cu} \qquad (2)$$

is proposed to explain this observation. A mathematical analysis based on this model was made in order to simulate a Cu/CuSO$_4$ system under pulsed current conditions by using a rotating disc electrode (RDE) as the cathode. The RDE was chosen mainly because of its desirable property of being a uniformly accessible surface [4, 5].

A detailed derivation of this hydrodynamic problem can be found in Levich's monograph [5].

2. Mathematical simulation

In this section, a mathematical simulation was set up to describe the rotating disc electrode system. The simulation of the RDE system under pulsed current conditions produces the theoretical response of current efficiency of copper deposition as a function of overpotential, rotation speed and characteristics of the applied pulsed potential.

For a RDE under pulsed potentiostatic conditions for a periodic reduction of Ions A and B in an electrochemical system described by the following reactions

$$\left.\begin{aligned} \mathrm{A + e^{-}} &\rightarrow \mathrm{B} \qquad (3)\\ \mathrm{B + e^{-}} &\rightarrow \mathrm{C} \qquad (4)\end{aligned}\right\}\text{at the disc electrode}$$

and

$$\mathrm{2B} \underset{k'}{\overset{k}{\rightleftharpoons}} \mathrm{A + C} \text{ in the solution} \qquad (5)$$

the concentration of A and B can be represented by the following equations

$$v_x \frac{\partial C_{\mathrm{A}}}{\partial x} + \frac{\partial C_{\mathrm{A}}}{\partial t} = D_{\mathrm{A}} \frac{\partial^2 C_{\mathrm{A}}}{\partial x^2} + kC_{\mathrm{B}}^2 - k'C_{\mathrm{A}} \qquad (6)$$

and

$$v_x \frac{\partial C_{\mathrm{B}}}{\partial x} + \frac{\partial C_{\mathrm{B}}}{\partial t} = D_{\mathrm{B}} \frac{\partial^2 C_{\mathrm{B}}}{\partial x^2} - 2kC_{\mathrm{B}}^2 - 2k'C_{\mathrm{A}}. \qquad (7)$$

The first term on the left-hand side of Equation 6 deals with the mass transfer of A by convection in the axial direction and the second term is the time variation of A. The first term on the right-hand side of Equation 6 governs the mass transfer of A by diffusion and the last two terms are related to the generation and consumption of A due to the homogeneous chemical reaction. The terms in Equation 7 have similar significance as those in Equation 6.

The boundary conditions are

$$\left.\begin{aligned} C_{\mathrm{A}} &= C_{\mathrm{A}}^{\mathrm{o}} \qquad (8)\\ C_{\mathrm{B}} &= C_{\mathrm{B}}^{\mathrm{o}} \qquad (9)\end{aligned}\right\}\text{at } x = \delta, t > 0$$

$$\left.\begin{aligned} C_{\mathrm{A}} &= C_{\mathrm{A}}^{\mathrm{o}} \qquad (10)\\ C_{\mathrm{B}} &= C_{\mathrm{B}}^{\mathrm{o}} \qquad (11)\end{aligned}\right\}\text{at } r = r_{\mathrm{o}}, t > 0$$

$$\left.\begin{aligned} \frac{\partial C_{\mathrm{A}}}{\partial r} &= 0 \qquad (12)\\ \frac{\partial C_{\mathrm{B}}}{\partial r} &= 0 \qquad (13)\end{aligned}\right\}\text{at } r = 0, t > 0.$$

In the present case, A stands for cupric ion and B for cuprous ion, and Equation 5 accounts for the disproportionation of cuprous ion and its reverse reaction.

The last boundary condition applies at the disc electrode surface, i.e., at $x = 0$

(a) At $0 < t \leqslant t_1$, $t_2 < t \leqslant t_3$, etc., during the ON period of the pulse, as illustrated in Fig. 1

$$i_1 = i_{\mathrm{o}_1}\left[\frac{C_{\mathrm{A}}^{\mathrm{s}}}{C_{\mathrm{A}}^{\mathrm{o}}}\exp(\alpha_{\mathrm{c}_1} F\eta/RT) - \frac{C_{\mathrm{B}}^{\mathrm{s}}}{C_{\mathrm{B}}^{\mathrm{o}}}\exp(\alpha_{\mathrm{a}_1} F\eta/RT)\right] \qquad (14)$$

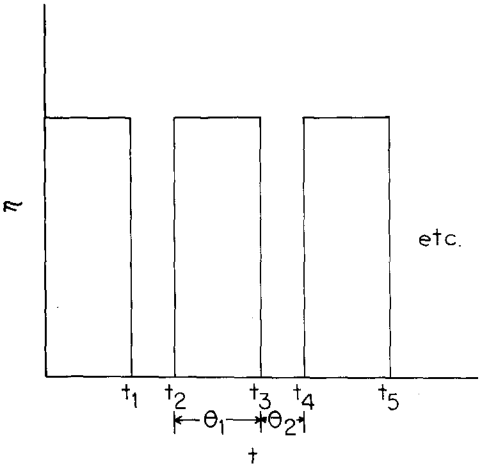

Fig. 1. Schematic diagram of potentiostatic pulses.

and

$$i_2 = i_{o_2}[(C_B^s/C_B^o)\exp(\alpha_{c_2}F\eta/RT) - \exp(\alpha_{a_2}F\eta/RT)]. \quad (15)$$

The form of Equations 14 and 15 has been adopted from those proposed by Newman [6]. We also have

$$\frac{D_A F}{1 - t_{Cu^{2+}}}\left(\frac{\partial C_A}{\partial x}\right) = i_1 \quad (16)$$

and

$$D_B F\left(\frac{\partial C_B}{\partial x}\right) = i_2 - i_1. \quad (17)$$

(b) At $t_1 < t \leqslant t_2, t_3 < t \leqslant t_4$, etc., during the OFF period of the pulse

$$i_1 = i_{o_1}[C_A^s/C_A^o - C_B^s/C_B^o] \quad (18)$$

$$i_2 = i_{o_2}[C_B^s/C_B^o - 1] \quad (19)$$

$$\frac{D_A F}{1 - t_{Cu^{2+}}}\frac{\partial C_A}{\partial x} = i_1 \quad (20)$$

and

$$D_B F\frac{\partial C_B}{\partial x} = i_2 - i_1. \quad (21)$$

The initial condition is

$$\left.\begin{aligned} C_A &= C_A^o \quad (22) \\ C_B &= C_B^o \quad (23) \end{aligned}\right\} \text{ at } t = 0, x \geqslant 0, r \geqslant 0.$$

Since an evaluation of both the exchange current densities and transfer coefficients simultaneously would involve a tremendous amount of experimental work and computer calculations, all transfer coefficients are assumed to have the value of 0·5 in this work, which is a reasonable approximation for most single charge transfer reactions [7]. Also, a value of $1{\cdot}1 \times 10^5 \, \mathrm{l\,M^{-1}\,s^{-1}}$ for k which has been reported by Iordanov and Trifonov [8] is used in the present calculation. Based on an equilibrium constant of the disproportionation reaction of 1×10^6 [9], k' is chosen to have the value of $1{\cdot}1 \times 10^{-1}\,\mathrm{s^{-1}}$.

Equations 6 and 7 subject to the boundary conditions, Equations 8–23 were transformed to finite difference form and solved on a digital computer. Concentration profiles of ions A and B in the vicinity of the rotating disc electrode were first obtained. The disc currents were then integrated from the local disc currents i_1 and i_2 by using Equations 14, 15, 18 and 19. The current efficiency which is defined as the percentage ratio of metal deposited to the theoretical amount of metal deposit computed from the total charge consumed by the system was then calculated according to the following equation,

$$\mathrm{CE} = \frac{2I_2}{I_1 + I_2} \times 10^2 \quad (24)$$

where I_1 and I_2 are the total disc currents for Reactions 3 and 4.

3. Experimental

An electrochemical cell made of Lucite was used in this study. The cell, shown schematically in Fig. 2, was 14 cm in diameter, 10 cm in depth and fitted with a tight cover.

The rotating disc electrode was driven by a motor (Model 2760-540, Heller) equipped with an electronic speed controller. This was connected through a flexible coupling to a Teflon shaft which rotated inside two ball bearings. A recess at the

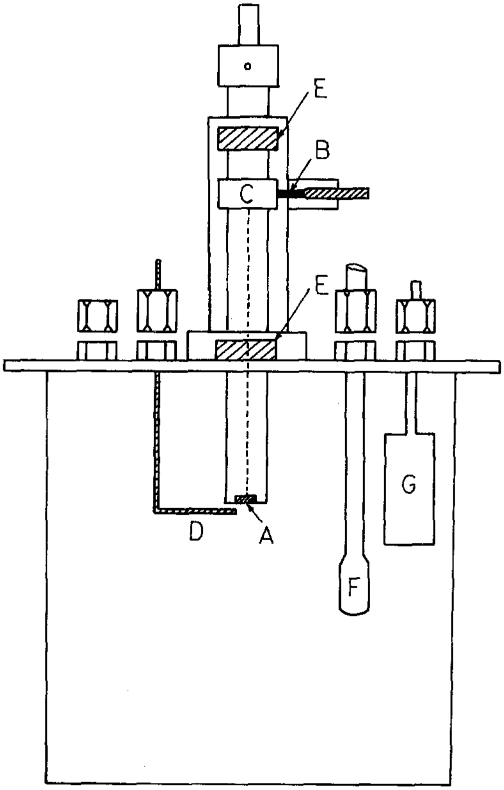

Fig. 2. Schematic diagram of cell with RDE assembly. (A: RDE, B: carbon brush, C: Cu ring, D: Cu reference electrode, E: ball bearing, F: sparger, G: Cu counter-electrode.)

end of the Teflon tube was used to give a tight press fit for the copper disc. The copper disc was in contact with a copper tube which served as a conductor between the disc and the external commutator. The radius of the disc electrode was 0·565 cm and the outer radius of the shaft was 1·272 cm. A copper plate (3 × 4 cm^2) was used as the counter-electrode and a copper wire was used as the reference electrode. The assumption that ohmic polarization was negligible was tested and confirmed. The potential difference between the reference and disc electrodes was measured when a current of 8 mA cm^{-2} was passed through the system. No observable change of overpotential was detected when the reference electrode was either rotated 90° parallel to the disc surface or lowered by 1 cm. Therefore, as long as the reference electrode was within 1 cm of the disc electrode, ohmic polarization was negligible.

A silver coulometer using a 1 M $AgNO_3$ solution connected in series with the main cell was used to measure the total charge consumed in the electrodeposition process. Pure silver plates (2 × 3 cm^2) were used as electrodes. The validity of the silver coulometer in pulsed plating has been confirmed by Lamb [10] and Fernando [11]. The anode compartment was separated from the cathode compartment by a sintered glass plate to prevent the anode slime from diffusing into the cathode compartment.

A combination of a potentiostat (Model 61 RS, Wenking) and a pulse generator (Type GSTP, Tacussel) was used to supply the potentiostatic pulse. The current was measured by the voltage drop across a precision resistor. Both the overpotential and current were recorded on an oscilloscope (Type 532-S7, Tektronix). The rise time for overpotential was observed to be less than 0·0002 s in all cases.

Reagent grade cupric sulphate and silver nitrate were used to prepare the 1 M $CuSO_4$ solution for copper deposition and the 1 M $AgNO_3$ solution in the silver coulometer. A piece of pure Cu was placed in the $CuSO_4$ solution for 24 hours for equilibration of the disproportionation reaction. Nitrogen was passed through the solution for one hour and a nitrogen atmosphere was maintained during the experiment.

Pulses with a number of characteristics were applied to the system. The ON cycle ranged from 0·005–0·01 s and the OFF cycle from 0·002–0·2 s. Constant motor speeds were maintained between 0–1100 rev min^{-1}. The disc overpotentials were kept at values between −300 mV and −100 mV with respect to the Cu reference electrode. When the electrolysis was terminated, the weight gains of copper disc and silver cathode were determined and the current efficiency was calculated accordingly.

The effect of exchange current densities (i_{o_1}, i_{o_2}) on CE and current density can be calculated from the mathematical model. It should be noted here that the average current density instead of the instantaneous current density has been found to be experimentally more reproducible. Consequently, under a given pulsed current condition, i_{o_1} and i_{o_2} can be estimated by measuring the CE and average current density of the plating system.

4. Results

Either duplicate or triplicate experiments were made for every set of experimental conditions. A

Table 1. Current efficiency of copper deposition under pulsed current conditions

η (mV)	θ_1 (s)	θ_2 (s)	ω (rev min^{-1})	*CE* (%)
−300	0·01	0·2	1100	85·6
−300	0·01	0·2	600	87·4
−300	0·01	0·2	250	88·5
−300	0·01	0·2	0	89·5
−300	0·01	0·1	250	89·9
−300	0·01	0·02	250	92·5
−300	0·01	0·002	250	93·7
−300	0·002	0·2	600	84·3
−300	0·002	0·2	250	84·8
−300	0·002	0·2	0	85·5
−300	0·002	0·1	250	86·2
−300	0·002	0·02	250	87·0
−300	0·0005	0·2	600	80·4
−300	0·0005	0·2	250	80·6
−300	0·0005	0·2	0	81·2
−300	0·0005	0·1	250	81·2
−300	0·0005	0·02	250	81·6
−250	0·01	0·2	0	88·2
−250	0·002	0·2	0	84·9
−250	0·0005	0·2	0	80·8
−200	0·01	0·2	0	86·5
−200	0·002	0·2	0	84·4
−200	0·0005	0·2	0	80·6
−150	0·01	0·2	0	85·8
−100	0·01	0·2	0	85·0

Table 2. Evaluation of exchange current densities

Experimental conditions				*Experimental data*		*Exchange current density*	
θ_1 (s)	θ_2 (s)	ω (rev min^{-1})	η (mV)	i_{avg} (mA cm^{-2})	*CE* (%)	i_{o_1} (mA cm^{-2})	i_{o_2} (mA cm^{-2})
0·01	0·2	250	300	8·0	88·5	0·0345	0·0240
0·0005	0·1	250	300	8·0	81·2	0·0348	0·0235
0·01	0·2	0	150	2·3	85·8	0·0333	0·0245
0·002	0·2	600	300	8·2	84·3	0·0342	0·0242
					Average	0·034	0·024

summary of averaged current efficiencies is given in Table 1.

The estimation of exchange current densities, i_{o_1} and i_{o_2} was based on four runs covering a wide range of experimental conditions. The measured current efficiency and the average current density were the parameters which were chosen to determine the values of i_{o_1} and i_{o_2}. The results are shown in Table 2.

Based on the average values of these exchange current densities, the theoretical response of current efficiency to different ON, OFF cycles, rotation speeds and electrode overpotentials are plotted in Figs. 3–5.

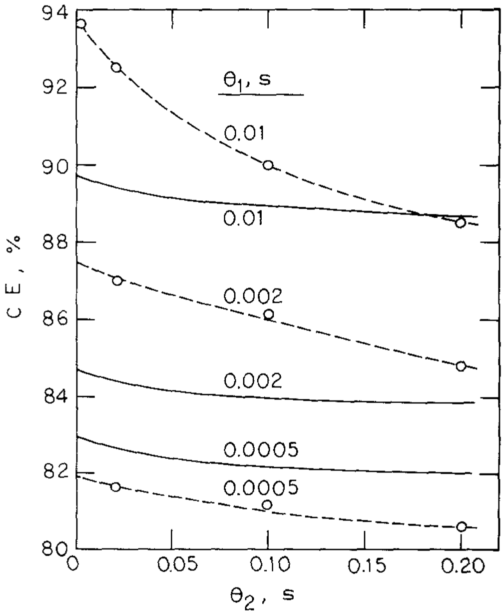

Fig. 3. Current efficiency of Cu deposition under pulsed conditions. (—— theoretical, ------ experimental).

5. Discussion

From Table 1 and Figs. 3–5 it can be seen that in a Cu/1 M $CuSO_4$ system under pulsed current conditions, with θ_1, θ_2, ω and η as the independent variables, the pulse time θ_1 has by far the greatest effect on the current efficiency. Considering the fact that the pulse time is usually about 0·001 s in galvanostatic investigations of electrode kinetics, the validity of applying this technique to reactions involving more than one step without any consideration of CE is rather questionable.

Electrical double-layer charging should not affect the CE although it can significantly change the boundary conditions. Meanwhile, to include double-layer effects in the calculations would make the problem extremely difficult to treat. An

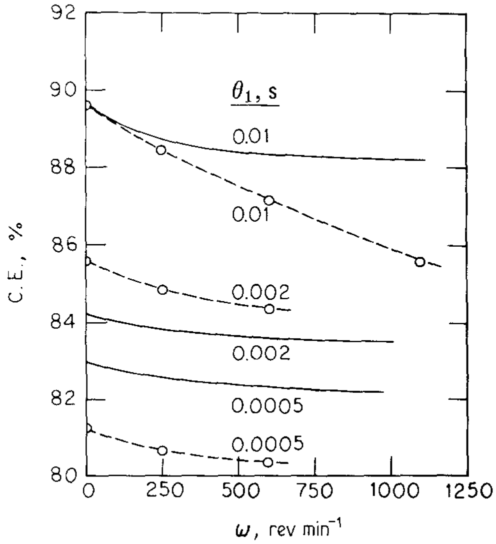

Fig. 4. Current efficiency of Cu deposition under pulsed conditions. (—— theoretical, ----- experimental).

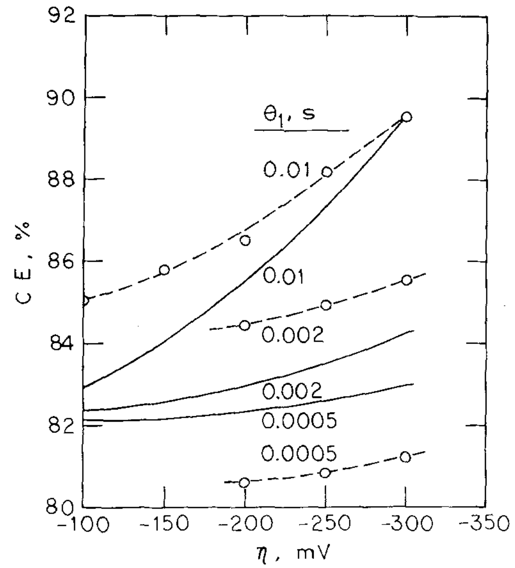

Fig. 5. Current efficiency of Cu deposition under pulsed conditions. (—— theoretical, ----- experimental).

examination of our data shows that transient effect due to double-layer charging is restricted to the initial 40% of the fastest on-time experiments [(0·0002/0·0005) x 10^2] and amounted to 2% for the slowest on-time experiments [(0·0002/0·01) x 10^2]. Consequently, double-layer charging was neglected in the analysis.

In comparing the experimental results to theoretical prediction, the measured change of current efficiency in response to change of θ_1, θ_2, ω and η is generally more pronounced than that calculated from the mathematical model. However, the difference between the predicted value and experimental data is within 3·5% in all cases and within 2% for 22 of the 25 observations. Considering the complexities of the model and the possible error of experimental measurements, the results can be considered to be satisfactory.

The exchange current densities i_{o_1} and i_{o_2} evaluated from the mathematical simulation of a Cu/1 M $CuSO_4$ system under pulsed current conditions are 0·034 mA cm^{-2} and 0·024 mA cm^{-2}. These are comparable in magnitude to the overall exchange current density quoted by Bockris [12] and by Parsons [13], which was also based on a Cu/1 M $CuSO_4$ system studied by Yuza and Kopyl [14].

An important element of this study is to note that the rate-determining step approach in chemical kinetics is useful only for steady-state systems. It is usually correct to state that in steady-state systems, the rate of the individual step is the same as that of the whole process. However, for unsteady-state situations such as copper plating by pulsed currents, the rate of individual step at a given moment is not necessarily equal to the rate of the overall process. The application of the theory of the rate determining step is consequently ambiguous in these systems.

Vetter [15] suggested considering each individual charge transfer step and its own i–η relation. However, only the basic equations for a much simplified case were available. Consequently, few experimental works which were based on this type of model could be found in the literature. Delahay [16] in his monograph briefly mentioned again the idea of treating each charge transfer step separately. However, to our knowledge this concept has not been developed to any appreciable extent. The concept of treating each charge transfer step individually as developed in this paper applies to systems at steady- as well as unsteady-state conditions. Also, the mathematical model based on this concept can explain both qualitatively and quantitatively the drop of current efficiency with a reasonable degree of accuracy.

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