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The electrochemical characteristics of a methanol stabilized electroless copper-plating solution

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The kinetics of electroless copper deposition onto non-metallic substrates have been examined at controlled potentials, using a rotating disc vitreous carbon electrode. The overall plating rate has been shown to be limited by the rate of the partial anodic process. The parameters controlling this retardation have been identified, and a model for the growth of electroless copper from active sites on the non-metallic surface has been suggested.

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1. Introduction

The practice of electroless plating onto non-metallic substrates and also the stoichiometry of the overall deposition reaction is well established, [1, 2]. Electrochemical studies have been largely confined to measurements of the mixed potential values and their relationship to the rate of the half-cell reactions [3, 4]. The arbitrary assumptions made in the derivation of these empirical rate equations and the difficulty of interpreting the results suggests that in order to obtain a complete understanding of the mechanism a more fundamental approach is necessary. In these laboratories, controlled potentials have been imposed on an activated carbon electrode and the current–potential behaviour of cathodic and anodic sweeps have been measured. An important feature of this technique is that the kinetics of the half-cell reactions can be estimated separately in the electroless solution without making any assumptions regarding the interaction of species at the mixed potential value.

2. Experimental procedure

A basic electroless copper plating solution containing 0·04 mol dm^{-3} Cu, 0·78 mol dm^{-3} HCHO, 0·1 mol dm^{-3} tartrate, 1·0 mol dm^{-3} NaOH and stabilized with 30% methanol was chosen for these studies [5].

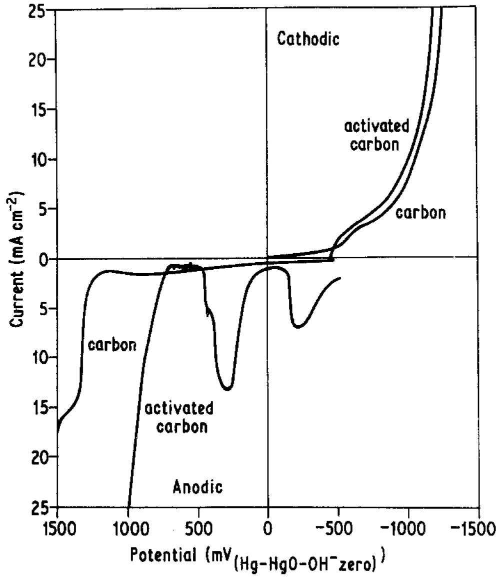

Fig. 1. Linear sweep curves for the anodic and cathodic components of the electroless reaction at carbon rotating disc electrodes. Sweep rate, 6·67 mV s^{-1}.

Vitreous carbon electrodes were activated with a deposit of palladium, by insertion into a 0·4 mol dm^{-3} $SnCl_2$ solution for 900 s followed by water washing, and finally activating in a 0·002 mol dm^{-3} $PdCl_2$ solution for 300 s. The activated electrodes were housed in a conventional 'H' type glass cell of 200 cm^3 capacity, with a 1 cm^2 Pt counter-electrode. Saturated calomel and Hg/HgO/OH$^-$ reference electrodes were used and all measurements were carried out at 298 K ± 3 K.

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Controlled potentials were applied to the electrode with a Chemical Electronics TR40/3A potentiostat. A linear sweep and waveform generator provided the external inputs to the potentiostat. Data from the potentiostat was recorded by either a Tektronix 564B storage oscilloscope or a Rikadenki BW133 *x–y* plotter.

3. Results

A preliminary investigation was carried out to ascertain the effects of electrode activation on the rates of the two half-cell reactions.

Starting from the mixed potential value, − 500 mV (Hg–HgO–OH^- zero), anodic and cathodic linear sweep curves have been obtained for activated and unactivated carbon electrodes. It can be seen from Fig. 1, that the anodic linear sweep curve for the activated carbon electrode shows two peaks whereas these peaks are absent in the case of unactivated carbon electrodes. In contrast to the anodic behaviour it can be seen in Fig. 1, that the cathodic half-cell reaction is not appreciably affected by activation of the carbon surface.

Methanol and formaldehyde are the two most important species available for oxidation in the electroless solution. The anodic linear sweep curve for the oxidation of formaldehyde (containing 11–14 wt% methanol) in the absence of any added methanol is shown in Fig. 2a. The curve is characterized by a stable and reproducible first peak, followed by a second peak which is irregular in shape and coincides with visible gas evolution from the electrode. In the absence of formaldehyde in the electroless solution the anodic linear sweep curve for the oxidation of methanol is shown in Fig. 2b. The curve shows a small peak at potentials between 0–100 mV, and a large peak which occurs at a more positive potential than the formaldehyde oxidation peaks. No peaks corresponding to the oxidation of the vitreous carbon substrate have been observed.

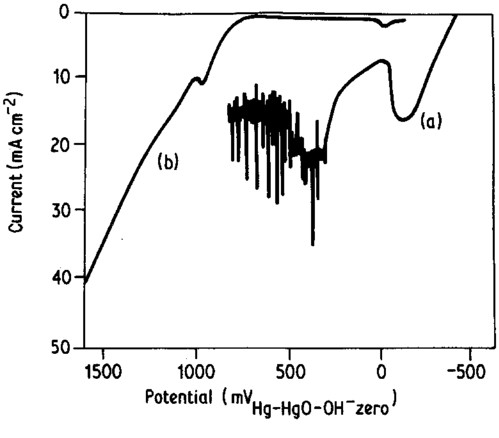

Fig. 2. Anodic linear sweep curves for the oxidation of (a) formaldehyde, (b) methanol, at an activated carbon rotating disc electrode. Solutions; (a) base solution without methanol, (b) base solution without formaldehyde. Sweep rate, 5 mV s^{-1}.

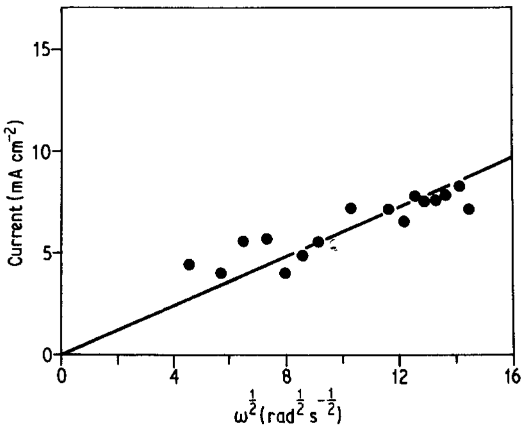

Fig. 3. Limiting current versus rotation speed for the deposition of copper at a sensitized and activated carbon electrode in the electroless solution. Sweep rate, 2 mV s^{-1}.

In contrast the cathodic linear sweep curves in the electroless solution starting from the mixed potential value show a rather indistinct peak at potentials between − 700 mV and − 800 mV before the onset of hydrogen evolution at the electrode, Fig. 1. In addition, values of the Cu^{2+} ion diffusion coefficient may be measured under the controlled diffusion conditions imposed by the rotating disc electrode technique. Equations for convective diffusion have been published [6] and the limiting current is given by

$$i_L = 0{\cdot}62nFAD^{2/3}V^{-1/6}\omega^{1/2}C^b$$

A plot of limiting current (i_L) against the square root of the rotational frequency ($\omega^{1/2}$) for the electroless system is shown in Fig. 3.

Finally, long-time pulse transients for cathodic pulses from the mixed potential value have been obtained. The curves show an initial fall, followed by a steady rise in current.

The effect of varying the solution concentration on the characteristic peak current values, Figs. 1 and 2, are shown in Fig. 4. The compo-

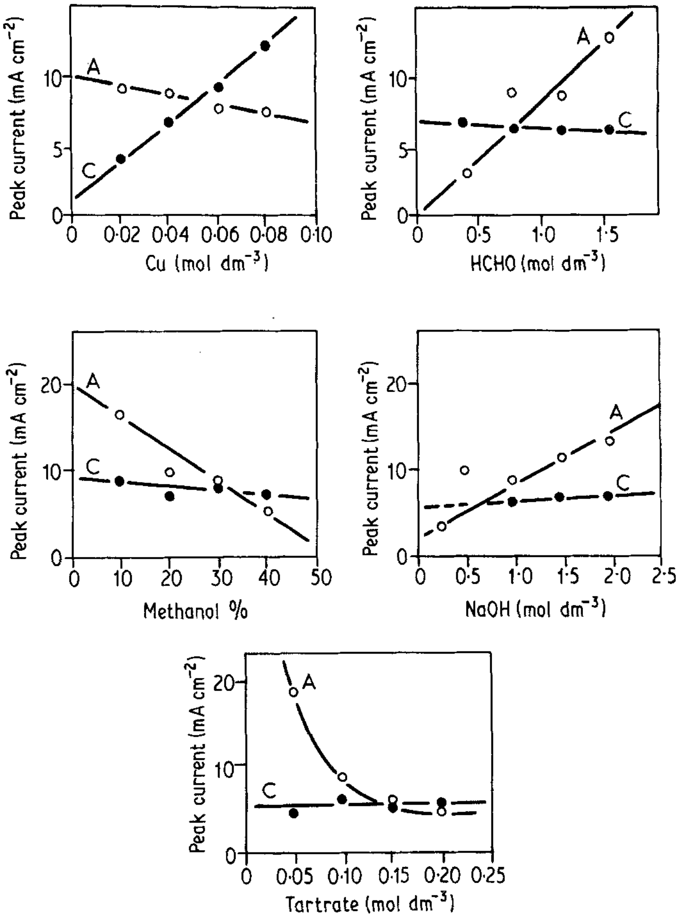

Fig. 4. Effect of solution concentration on the peak current values. Base solution: 0·04 mol dm^{-3} Cu, 0·78 mol dm^{-3} HCHO, 1·0 mol dm^{-3} NaOH, 0·1 mol dm^{-3} tartrate, 30% methanol. Sweep rate, 3·3 mV s^{-1}. (A, anodic; C, cathodic)

sitions of the Cu, HCHO, tartrate and NaOH species were altered systematically over a limited range around the composition of the base solution. No attempt was made to control the ionic strength of these solutions since it was considered that maintaining constant ionic strength by buffering the solution would not significantly alter the general trends observed.

4. Discussion

It has been suggested [7] that the anodic and cathodic reactions occur together on the electrode surface at the mixed potential value. The controlled potential studies of the electroless copper cathodic half-cell reaction have shown that at short times the results are consistent with published reports [7–9] of the mechanism of electrolytic copper deposition, for which the cupric/cuprous change has been suggested as the rate-determining step. The pulse transients obtained are similar to those observed for the electrolytic deposition of copper from acidic solutions [9] in which it was suggested that the mechanism involves the nucleation and three-dimensional growth of copper at a limited number of the cathodic sites. From the plot of limiting current versus the square root of the rotational frequency, Fig. 3, the value for the diffusion coefficient of the Cu^{2+} ion in the electroless solution has been shown to be 0·15 x 10^{-6} cm^2 s^{-1}. A value of $D_{Cu^{2+}}$ = 3·95 x 10^{-6} cm^2 s^{-1} has been obtained [9] for the electrolytic deposition of copper from an acidic solution of copper sulphate. The difference in the values of the diffusion coefficients for $D_{Cu^{2+}}$ may be attributed to the formation of a copper complex in the electroless solution. Measurements of the peak current have shown that it is the anodic half-cell reaction which has the major effect on retarding the overall rate of the electroless process. Controlled potential sweep measurements of the anodic half-cell reaction have shown that the rate of oxidation of formaldehyde which is present as the methylene glycol ion [10] is substantially increased when the carbon electrodes are activated, Fig. 1. In contrast the rate of methanol oxidation appears to be independent of the presence of palladium on the carbon surface, Fig. 2. In addition it can be seen that whereas formaldehyde is oxidized at a copper surface, methanol is probably oxidized on Cu_2O, Fig. 2. It is therefore reasonable to assume that the peaks observed during a linear anodic sweep from the mixed potential value are due to the oxidation of formaldehyde at the active sites. It is suggested that the first peak current value is due to the rapid blocking of the anodic sites by the adsorption of the intermediate products formed during the oxidation of formaldehyde and/or the adsorption of methanol. The rate of the anodic half-cell reaction, as measured by the peak current value, will depend largely upon the amount of free formaldehyde or methylene glycol anion available for oxidation at the surface of the electrode. Such pre-electrochemical reactions and also the possibility of dissociative absorption of species on the electrode may account for the observed variation of the anodic peak current value with sweep rate, which cannot be explained by a simple electron-transfer model. Although the mechanism for the copper deposition at very short times remains obscure it is clear that at long times the rate of deposition is controlled by the rate of oxidation of the methylene glycol anion at the forming copper surface. It is well established that copper oxide is present on copper electrodes in alkaline solutions [11] and the characteristic incubation period observed in electroless plating is probably due to the finite time required to reduce this oxide layer. Cupric ions which are present in the solution as a complex diffuse through the electrical double layer to the cathodic sites on the copper surface. The cupric ion may be present at the cathodic sites as a complex or it may be stripped or partly stripped of its complexing molecules as it passes through the double layer. Simultaneously formaldehyde in the form of the methylene glycol anion, diffuses to the adjacent anodic sites on the surface. Electron transfer leads to the deposition of copper at the cathodic sites, and the electrically equivalent formation of oxidation products at the anodic sites. As copper deposition proceeds by electron exchange the lateral growth of centres is effectively prevented by the presence of blocking species at the anodic sites. Additional deposition is restricted to those areas of copper which have either not been oxidized to Cu_2O or blocked by the oxidation products of formaldehyde or stabilizer molecules. A schematic diagram of the development of a single copper centre is shown in Fig. 5. At longer times the rate of growth of these initial copper centres will decrease and this prediction is consistent with the electron microscopic observations of previous workers [12] where it has been shown that the initial copper centres reach a limiting size after which new centres nucleate on the surface. Eventually growing islands will meet and bridge over the parts of the surface on which growing copper centres are absent.

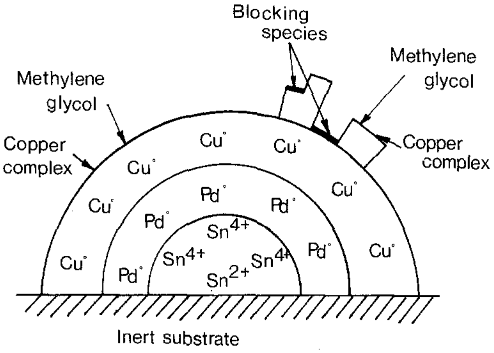

Fig. 5. Suggested model for the growth of chemically deposited copper onto activated non-metallic substrates.

5. Conclusions

It has been shown that rotating disc potentiostatic techniques can be successfully applied to the study of electroless metal deposition reactions onto non-metallic surfaces by using activated carbon substrates. It has been possible to show that there is no limit to the rate of the cathodic metal deposition process, and that the net rate of the electroless deposition is controlled only by a retardation of the anodic process. Further work to find suitable unblocking agents which will enable high plating rates to be sustained for long periods of time is being carried out.

Acknowledgements

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