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An electrochemical mass transport sensor to study agitation in electroplating processes

S. A. AMADI, D. R. GABE

IPTME, Loughborough University of Technology, Loughborough, LE11 3TU, Great Britain

M. GOODENOUGH

Lea-Ronal (UK) Ltd., Buxton, SK17 9SS, Great Britain

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A sensor based on limiting current density characteristics of a wire tip electrode has been shown to be capable of measuring local variations of agitation and its effect on coating thickness variations during electrodeposition. The effectiveness of agitation is expressed as an enhancement factor.

1. Introduction

The concept of sensors for electroplating process control is not new but has become more closely defined in recent years, substantially due to the initiatives of Turner [1]. The use of sensors has traditionally been to monitor the process solution through pH, temperature, conductivity and metal ion concentration, but using electronic feedback systems a considerable degree of automation is now feasible [2, 3]. The need to measure local or general mass transport rates arises in several ways but it is not always necessary to measure such rates in absolute terms. For example, a change in mass transport, usually an increase, may often be quite adequately considered as a degree of process enhancement or as an enhancement factor. This may be caused by, or related to, several distinct situations, i.e. enhancement due to:

(a) increased diffusion rates as a consequence of increased solution temperatures;
(b) increased cathode surface areas caused by electrodeposit roughening as nodular or dendritic growth develops; and
(c) increased agitation which decreases the cathode diffusion layer thickness.

This study is concerned with the third possibility and has adopted an established strategy which is well-developed in the other cases.

2. Principle of the method

The key to the method is the well-known Nernst limiting current equation

$$I_L = \frac{zFCDA}{\delta} \tag{1}$$

Because the method employs directly measured limiting currents, this equation will be preferred to a mass transfer coefficient equation in this context which, for two sets of experimental conditions, can give rise directly to an enhancement factor (EF):

$$EF = I'_L/I''_L \tag{2}$$

where $I'_L > I''_L$. When one parameter only is varied to produce enhancement the following relationships apply with respect to situations (a), (b) and (c) already cited.

$$\frac{I'_L}{I''_L} = \frac{D'}{D''} \tag{3a}$$

$$\frac{I'_L}{I''_L} = \frac{A'}{A''} \tag{3b}$$

$$\frac{I'_L}{I''_L} = \frac{\delta''}{\delta'} \tag{3c}$$

If that parameter is temperature both D and δ may be affected by changes of viscosity so a more correct form would be

$$\frac{I'_L}{I''_L} = \frac{D'\delta''}{D''\delta'} \tag{3d}$$

The principle has bene used successfully in several instances. Considering first the case of electrode surface area, a previous study used this approach to measure surface areas of deliberately machine-roughened cylinder electrodes and a comparison was favourably made with geometrical measurements of the true surface area [4, 5]. An analgous method due to Puippe [6, 7] is the basis of the DIM instrument for assessing areas of intricate electronic or jewellery components prior to electroplating. In the case of agitation or flow rates, a change in I_L has been suggested as a means of assessing the degree of flow [8] although no data have apparently been published.

These two types of study have led to the idea of using a limiting current technique with a small probe or sensor electrode to assess the degree of agitation (or flow) within a large reactor vessel or electroplating cell. While akin to a microelectrode technique, the practicable size of the electrode is much bigger than

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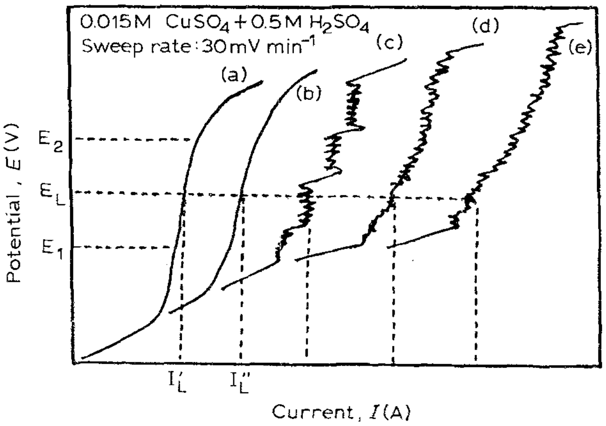

Fig. 1. Polarization curves showing limiting currents values at increasing vibratory agitation rates and the equivalent limiting potential, E_L, $E_L = (E_1 + E_2)/2$.

that used elsewhere: for example the studies of Wragg *et al.* [9] which employed surface-flush microelectrodes to study these flow patterns.

3. Experimental details

In order for the sensor to be used quickly and effectively a rapid method of measuring the limiting current I_L is required; in this study of agitation, a model acid copper sulphate solution has been employed whose mass transport characteristics have been determined previously. Gabe and Makanjuola [10] have shown that by establishing the potential/current curve in the vicinity of the limiting current a potential E_L, equivalent to the limiting current I_L, can be defined (see Fig. 1) so that when applied potentiostatically the limiting current value can be quickly measured, especially when the degree of agitation employed is substantially increased. By monitoring the current/time function (see Fig. 2) steady state conditions exist after 10–40 s, after which the current rises slowly as rough growth develops. As the agitation is increased the minimum time reduces to 10 s (Fig. 2) and the precise value of I_L becomes less certain (Fig. 1) as powdery growth can commence during the relatively slow scanning rate.

The solution comprised 0.3 M $CuSO_4$ and 2.25 M H_2SO_4 at 18°C. The principal characteristics of the solution are its diffusion coefficient ($D = 5.84 \times 10^{-6}$ $cm^2 s^{-1}$) and its kinematic viscosity ($\nu = 1.0184 \times 10^{-2} cm^2 s^{-1}$).

Plating tanks of up to 25 dm^3 volume were employed and the cathodes were flat sheets of stainless steel suspended vertically to simulate typically printed circuit boards in a production unit. Agitation was achieved by conventional air agitation or vibratory agitation as recently described elsewhere [11, 12], both applied at the centre-bottom of the tank. Limiting current values measured in the tank without agitation were used as baseline values (I_L) relative to which enhancement factors (*EF*s) were obtained as in Equations 2 and 3c.

The sensor was typically a small wire-tip electrode with an associated Luggin probe or sintered glass remote reference electrode, i.e. a two-electrode assembly (see Fig. 3). Both calomel (SCE) and mercurous sulphate (MMS) reference electrodes have been used. The two-electrode probe can be moved around the tank and its position recorded in three dimensional coordinates. The counter electrode was a large flat sheet best placed at a tank wall so as not to interfere with the developed pattern of agitation. Alternatively it can be placed adjacent to the work pieces and 'dead' agitation zones identified. A X-ray fluorescence method of thickness testing on the sheet cathodes (Fischer Instruments) was employed to make a comparison of actual thickness and equivalent thickness values assuming > 90% cathode current efficiency.

4. Results

The sensor has been used to measure the variation of agitation in large plating tanks, produced by nonsymmetrical or localized agitators, which lead in industrial processes to variable degrees of electrodeposit thickness on large cathode work pieces. Such sources of variation are often attributed to 'throwing power' effects but in practice they may be due to both true throwing power effects and local variability in agitation due to flow shielding by irregularly shaped or contoured cathodes. The sensor has also been used to compare agitation techniques in

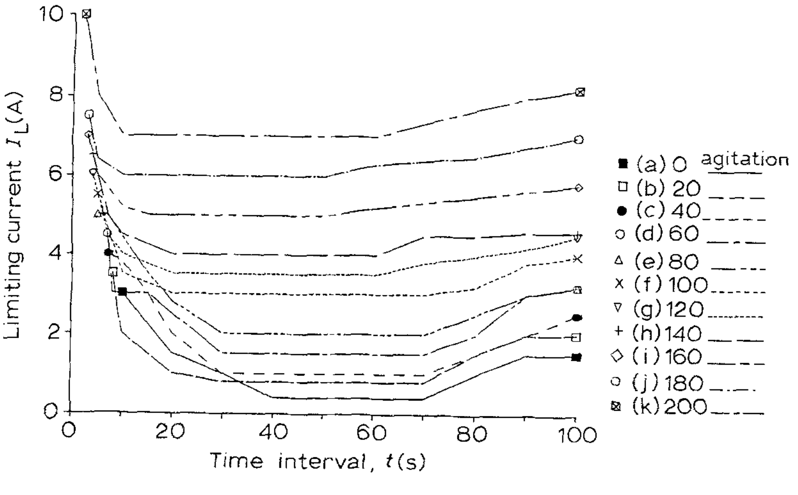

Fig. 2. Relationship of limiting current and time using the sensor electrode technique at different degrees of vibratory agitation under potentiostatic control.

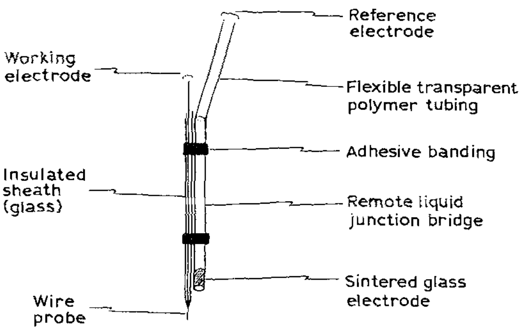

Fig. 3. Typical schematic representation of the sensor electrode (working electrode) and the reference electrode used in this study.

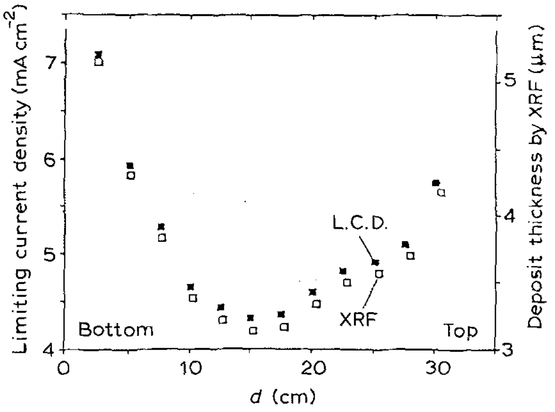

Fig. 4. Limiting current density and metal thickness distribution profiles from top to bottom of a 25 litre electroplating tank. LCD – sensor method; XRF – X-ray fluorescence analysis.

terms of process rate enhancement, this being one particular reason for the use of agitation.

In these experiments variations in the degree of agitation in the tank have been measured from top to middle to bottom and from side to centre to side. But initially a calibration was attempted in relation to deposit thickness by use of a large vertical sheet, simulating a printed circuit board, on which the coating thickness was measured by X-ray fluorescence after electrodeposition at a normal current density (e.g. 10 mA cm^{-2}). Figure 4 shows the very good agreement which was obtained. It also illustrates that for vibratory agitation marked enhancement occurs at the bottom, relatively little at the middle and rather more at the top near the meniscus interface. By using the sensor in small increments of height from top to bottom and variable vibratory agitation rate, a very detailed pattern of agitation could be obtained (Fig. 5).

Variation across the tank (corner–centre–corner) was investigated in a similar manner using three vibration agitation levels and the probe in the bottom, middle and top positions (Figs. 6–8). It can be seen that the tank wall 'drag' effect extends for about 7 cm and is more marked at the middle level (Fig. 7). These figures also illustrate how the degree of agitation can be interpreted as an enhancement factor. If the same effect is studied on a side–centre–side basis the 'drag' effect appears more marked (Fig. 9) with a very sharp peak of vibratory agitative effectiveness at the centre.

It is interesting to compare air agitation in this context. This is not the place to consider air agitation characteristics in detail but it is worth noting that air agitation can produce a more even or uniform effect but that the degree of enhancement does not increase markedly with air flow rate for a given pattern of air bubble distributor (Fig. 10). Figure 10 demonstrates that below 3 dm^3 min^{-1} the bubble release or evolution is spasmodic or erratic giving rise to bursts of activity creating an impression of high mass transfer at 3–4 dm^3 min^{-1}. But when a 'steady state' of bubble agitation has developed at 4–5 dm^3 min^{-1}. The pattern of agitation is remarkably uniform giving limiting current density in values of 12.05–12.24 mA cm^{-2} which represents a very narrow range. This is found for air flow rates of 4.5–10 dm^3 min^{-1} which is a wide range of flow rates. Thus it may be considered to be extremely good for uniformity but relatively poor for increasing deposition rate.

5. Discussion

The variation of agitation within a large electroplating tank has always been known in a qualitative manner and the art of jigging irregularly shaped components to produce evenly coated products is one obvious manifestation of this knowledge. To establish the effect quantitatively is more difficult, although various throwing power cells (Haring, Hull) purport to do this in various ways. But none effectively include agitation as a parameter. Similarly, the use of limiting current methods is well-established as a means of assessing

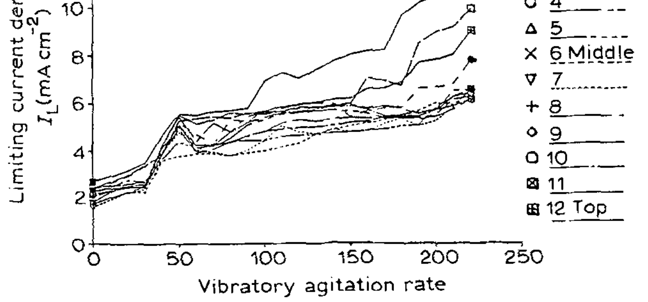

Fig. 5. Limiting current density distribution profile, determined by sensor, from top to bottom of a vertical flat sheet cathode of various vibratory agitation rates.

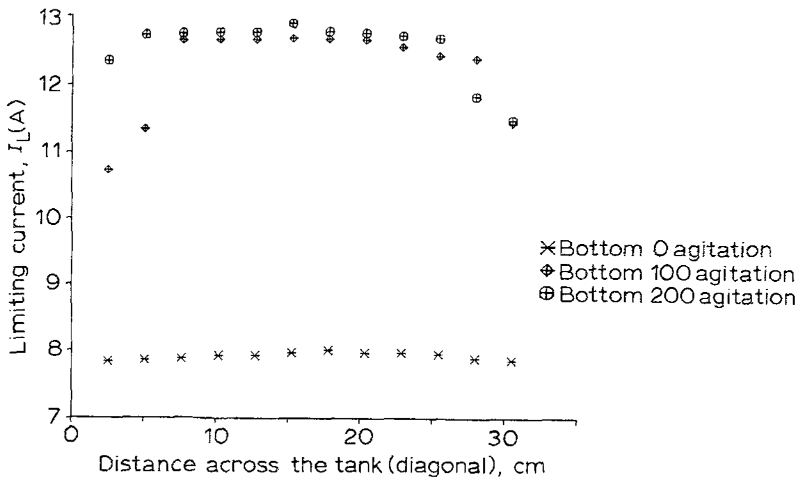

Fig. 6. Limiting current density distribution along a tank diagonal for a vibratory agitated electrolyte: bottom positions.

reactor performance or overall cathode deposition rates edge effects being clearly recognized as edge build-up or edge burning. The equivalence of deposit thickness and current density is implicit in the use of the Hull cell but when limiting current densities are employed, the current efficiency is invariably invoked as a reason for caution. In this light Fig. 4 demonstrates a remarkable level of agreement. No specific claim for the Faradaic equivalence is made but it should be noted that the discrepancy is attributable primarily to current efficiencies of less than 100%. It should be noted that the limiting current density technique is designed to be one near 100% efficiency because the selection of an acid copper sulphate electrolyte and the selection of an appropriate control potential (−0.85 V/SCE) is an attempt to operate under conditions where hydrogen evolution has not commenced (see Fig. 1). Thus the sensor technique is believed to correlate well with deposit thickness. Reproducible re-use of the sensor depends on removing the metal deposited each time; this is generally possible with powdery deposits. Alternatively a stainless steel wire allows acid dissolution with nitric acid without itself being attacked.

Investigation of the pattern of agitation within the electroplating tank has revealed several interesting features, some of which are already known in a qualitative manner. Thus wall 'drag' effects are well appreciated and components are kept towards the centre of a tank. Equally components are suspended in the middle of the tank in depth terms on the basis that agitation

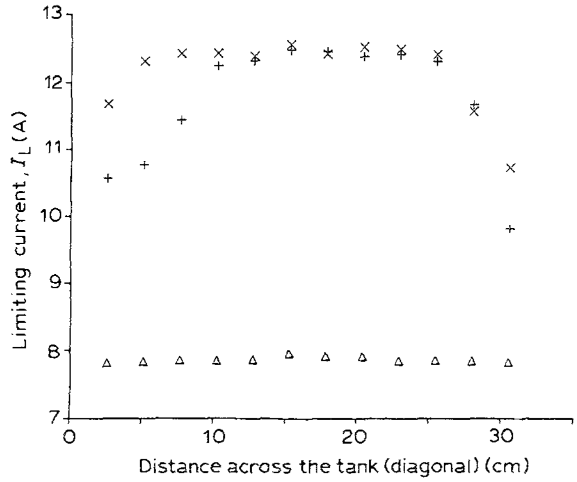

Fig. 8. Limiting current density distribution along a tank diagonal for a vibratory agitate electrolyte: top positions. (△) 0 agitation; + 100 agitation and × 200 agitation.

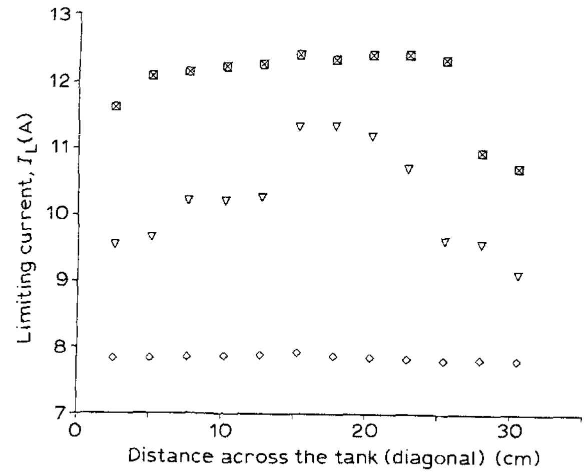

Fig. 7. Limiting current density distribution along a tank diagonal for a vibratory agitated electrolyte: centre positions. (◇) 0 agitation; (▽) 100 agitation and (⊠) 200 agitation.

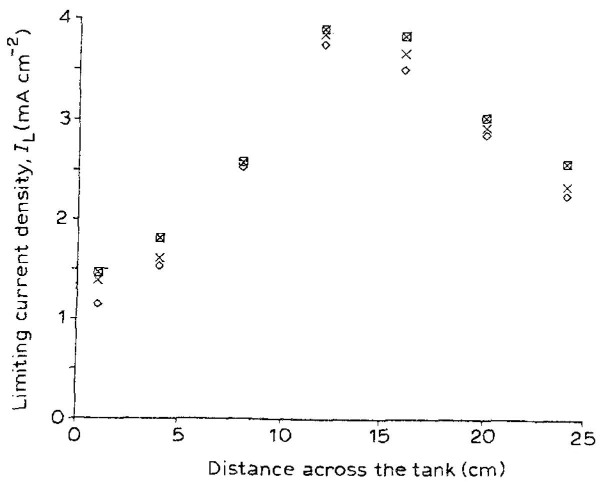

Fig. 9. Distribution profile of limiting current density across the tank (side to side) for three vertical positions. × top; ◇ centre and ⊠ bottom.

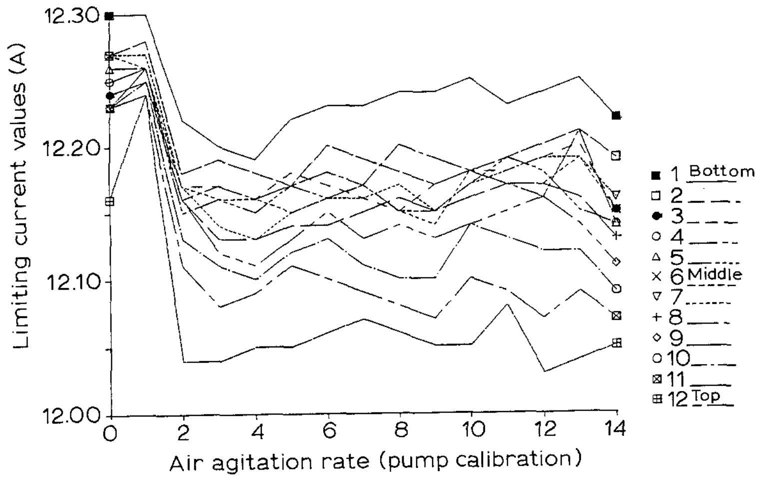

Fig. 10. Limiting current distribution profile, determined by sensor, from top to bottom of a vertical flat sheet cathode at various air agitation rates.

at the top and bottom is atypical. The nature of this atypical behaviour is only guessed at however.

The bottom of the tank is clearly well-agitated with both vibratory and air techniques because it is near the source of agitative power. A damping effect within the solution is also recognized as higher positions are taken. However, enhancement at the top is not generally appreciated but here vibratory and air agitation can be distinguished.

It has been pointed out elsewhere [11, 12] that to be successful vibratory agitators must be designed to allow circulatory eddies to develop: thus the vibrator plate must leave a substantial gap between itself and the tank wall. However, it is equally important that the vibratory waves must be able to reflect off the top electrolyte interface or surface in order to circulate outwards; this they do with a consequent increase in local agitation near the solution surface. In contrast, air bubbles do not circulate but, on rising to the surface, disperse into the air through the interface and if a bubble raft forms, an effect especially prevalent in chromium plating solutions where hydrogen gas is also present, plating is substantially inhibited and not enhanced. But air agitation does have the virtue of giving a more uniform level of agitation throughout the tank.

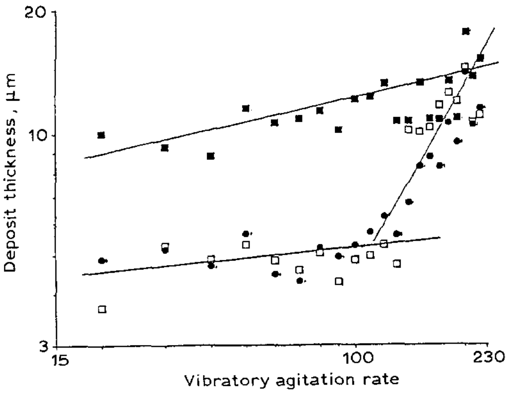

Fig. 11. Effect of vibratory agitation rate on deposition thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm^2 and plating time = 20 min per sample at constant potential. ■ bottom; □ top and ● middle.

Table 1. Enhancement factor as a measure of agitation

	EF
Cathode reciprocation	1–2
Air agitation	2–5
Vibratory agitation	2–10

For this reason it is simplistic to assume that a common mass transport analysis of the whole tank can be made for vibratory agitation. Closer examination of the data in Fig. 5 reveals two distinct mass transport patterns which are shown more clearly in Fig. 11. These may be related to patterns of turbulence which become prevalent at higher degrees of agitation, often above a critical value, but which also depends on the geometrical restrictions of flow and proximity to the source of agitation.

The degree of enhancement is a measure of the effectiveness of the agitation technique in relation to high speed electrodeposition. On this basis air is singularly poor although somewhat better than the usual gentle lateral cathode bar reciprocation which is merely designed to eliminate stagnation. Ranges of enhancement factor, representing variation within the tank and also variation with degree of agitation are listed in Table 1.

Acknowledgements

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