Journal of Applied Electrochemistry **30**: 457–466, 2000.

Effects of air agitation on conductivity in acid copper electrodeposition solutions

M. WARD, C.J. ROBERTS and D.R. GABE
IPTME, Loughborough University, LE11 3TU, Great Britain

Received 23 December 1998; accepted in revised form 29 September 1999

Key words: acid–copper, agitation, conductivity, throwing power, voidage

Abstract

The effects of air agitation on electrolyte conductivity have been considered. Experimental data obtained from a conductivity probe was found to be comparable to theoretical models for conductivity which show that localized reductions of 20–30% are quite normal in an acid copper electrolyte. Such nonuniformity within an electroplating tank could be one cause of the throwing power/metal distribution variations which are normally attributed to surface irregularities or poorly designed agitation systems. These aspects have particular bearing for printed circuit board (PCB) manufacture where consistency in electrodeposition is paramount to ensure low defect or failure rates, especially within high aspect ratio through-holes.

List of symbols

D	diffusion coefficient of species (mol m^2 s^{-1})
L	characteristic length
R_C	relative conductivity
u_∞	free stream velocity (m s^{-1})
x	characteristic dimension

Greek letters

ε_g	gas voidage fraction
κ	effective conductivity (S m^{-1})
v	kinematic viscosity (m^2 s^{-1})
$d\eta/di$	slope of polarization curve (V A^{-1} m^2)

Subscripts

L, g	liquid, gas phase
0	gas-free solution

1. Introduction

Conductivity is a physical property of an electroplating solution and is dependent upon chemical constituents affecting ionic mobilities. Furthermore, since the effect of temperature is primarily through ion diffusive mobility, it follows that elevated temperature leads to increased conductivity. Consequently, solution motion does not affect conductivity *per se* and its practical attainment is much more a consideration of the electrical energy employed and the effectiveness of increasing deposition rates. The chemical characteristics and approaches to conductivity optimization have recently been discussed [1, 2] and will not be further explored in this paper.

Solution agitation in industrial processes is frequently carried out by air sparging or bubbling. The reasons for this are largely historical but can be considered as simplicity and cost. However, the presence of air creates a two-phase (liquid–gas) medium whose conductivity is lower than the original solution, since air is clearly a resistive second phase. Although this phenomenon has been recognised and occasionally studied [1–3], there has been minor impact on the electroplating trade who continue to use air, except for solutions liable to be oxidised (e.g., stannous tin solutions) and those where higher speed deposition is required. The two-phase nature has been studied previously [4, 5] and the simplest representation of the solution conductivity is the ‘rule of mixtures’:

$$\varepsilon_L \kappa_L + \kappa_g \varepsilon_g = \kappa \tag{1a}$$

and

$$\varepsilon_L + \varepsilon_g = 1 \tag{1b}$$

hence,

$$(1 - \varepsilon_g)\kappa_L + \kappa_g \varepsilon_g = \kappa \tag{1c}$$

This demonstrates a linear relationship between air voidage and conductivity and will be used as the simplest form of equation for predicting conductivity.

This research has arisen from the need to provide deposition conditions conducive to high quality coverage and through-hole continuity on PCBs. The Wagner number (Wa) has often been used to define this ability [6–8]:

$$Wa = \frac{\kappa}{L}\left(\frac{\mathrm{d}\eta}{\mathrm{d}i}\right) \quad (2)$$

For a PCB electrodeposition process, L could be the depth of a very narrow through-hole. Since throwing power is an indication of the electrolytes ability to deposit uniformly on an uneven cathode surface and the Wagner number is used to describe even current distribution in a recess region (i.e., a through-hole), then maximizing both factors is beneficial to uniformity of deposition. Previous work has explored the maximisation of conductivity through optimised solution composition [6–8]; this work explores the characteristics of air agitation and the possible use of alternatives including pumped fluid or eductor agitation.

2. Experimental details

The experimental arrangements have been described in detail elsewhere [2]. In brief, a Jenway (model 4200) meter was used to measure the conductivity of 25 litres of a 'model' acid copper electrolyte (0.010 M $CuSO_4$, 0.4 M H_2SO_4). The choice of electrolyte was necessary to ensure conductivity was less than 200 mS cm^{-1}, the upper limit of the Jenway meter. Note that whilst a typical electrolyte for PCB production would contain 0.3 M $CuSO_4$, 2.2 M H_2SO_4 and have $\kappa_0 = {\sim}550$ mS cm^{-1}, the effects of conductivity reduction through agitation will occur in similar proportions in either electrolyte. The solution was held in a 40 litre capacity tank fitted with a central, longitudinal air sparge system of traditional format [4]; high and low air flow rates were achieved using one or two pumps and a pumped fluid (i.e., air free) system was also considered.

The Jenway conductivity probe (of carbon, four-plate construction) was directly exposed to the process electrolyte, thereby enabling continuous measurement of the local conductivity level. Individual measurements were recorded on a time averaged basis to take into account any transitory fluctuations. Each measurement was performed sequentially as the probe was moved on Cartesian coordinates at three different depth-planes within the tank, enabling a net volume of approximately 15 litres to be studied, as shown schematically in Figure 1. Data was collated to produce three-dimensional 'maps' of the conductivity variations at each level within the tank; results were compared to previous work which evaluated conductivity at a fixed point under increased air flowrates [1, 2].

Results have previously been obtained for a number of other solutions [1, 2] but only those relating to the model solution are discussed here; agitation characteristics within acid copper electrolytes have also been reviewed elsewhere [4–9].

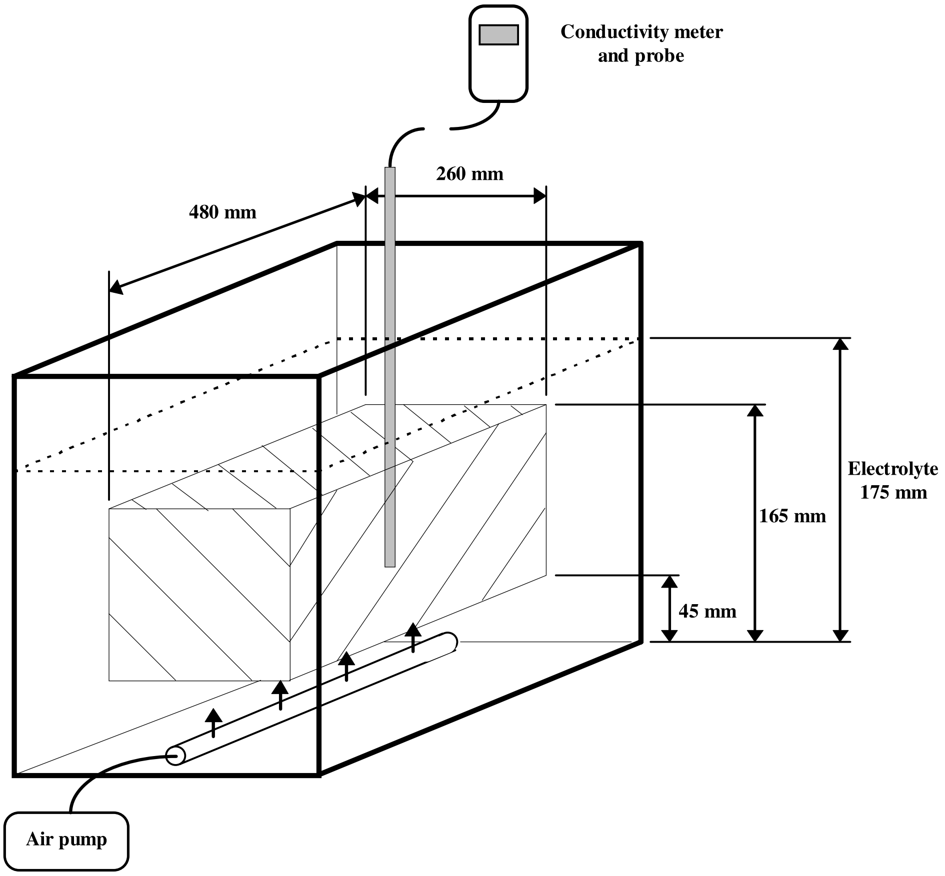

Fig. 1. Schematic of experimental apparatus showing air sparge tube, conductivity probe and working envelope (shaded area).

3. Results and discussion

3.1. *Agitation and conductivity mapping*

Using the methodology employed earlier for agitation 'mapping' [9], the graphical results obtained from studying local conductivity differences are presented in Figures 2–6. Note that these figures show the degree of variation across each plane, from the nominal value (135 mS cm^{-1}) at the edge to the central, agitation-influenced values.

This research has demonstrated that both the degree and locality of agitation can influence conductivity and, therefore, the throwing power, as expressed by the Wagner number. Two features of significance shown are (i) variation due to air pump connection and sparger design, and (ii) variation due to height within the electroplating tank. The consequences of these two points need to be considered in a full scale electroplating process. The first point is demonstrated by results obtained at the 45 mm plane, i.e. immediately above the sparger. The degree of conductivity reduction is associated with the voidage fraction of the bubbles, which are in turn a function of the: input air pressure; sparge exit-hole diameter and position along the sparge pipe. For example, Figure 2(c) shows that when a single air pump was connected to the left hand side of the sparge pipe, pressure differential along the pipe produced unequal agitation/conductivity between either end of the tank. Conductivity was equalised at this plane by enlarging the exit-hole size from 1 to 1.4 mm and increasing the airflow rate (Figure 3(c)); this lowered the pressure drop along the sparge tube by reducing resistance to escape of the air into the electrolyte. When a low pressure, dual pump system was used, two local regions of high agitation but low conductivity were created (Figures 4b and c); again, increased flow rate (Figure 5) and hole size (Figure 6) reduced this effect. In practice, determining whether pressure differential is eliminated would only be possible using either a conductivity probe, or by measuring coating thickness distribution created by non-uniformity in throwing power. Consideration should be given to sparge designs whereby exit-hole sizes change between the ends and middle of the tube. Bubbles have previously been photographed to show their emerging shape and size [4, 5] and that volume fraction becomes incorporated in the conductivity profile.

Conductivity variation between individual measuring planes is clearly evident in Figures 2–6, the degree of variation being related to both the amount of agitation and the locality across the measuring plane. The effect may be attributed to the growth and dispersion of bubbles rising through zones of decreasing hydrostatic pressure. The sideways dispersion of bubbles occurring at increased height above the sparge pipe had the effect of reducing voidage from the high degree immediately above the sparge exit-holes; bubble incorporation into an increased electrolyte volume meant that conductivity shifted towards its unagitated value, as predicted by the 'rule of mixtures' approach (Equation 1). Of course, in an industrial installation with jigged components these ideal bubble streams are interrupted and usually create some small, localised additional turbulence. This is believed to be helpful provided recesses can be prevented from becoming dead zones and thereby places of low deposit coverage or thickness.

A commercial process operating at maximum agitation rate could be likened to the variation recorded in Figure 6. Minimising this variation between levels needs to be addressed in cell/agitation design so that throwing power remains uniform with height and position in tank; a working 'envelope' for jigging of components should be considered. Furthermore, although the narrow cross-section of a PCB could be positioned centrally above the sparge tube, an irregular shaped component would cause some disturbance to the air flow and create a different conductivity distribution to the ones reported here.

In terms of absolute conductivity loss, 20–30% reductions have been recorded in Figure 7, based on the work of Guvendik [10] using a variable rate air pump, where the high air pressure and large exit-hole size increased the level of air voidage. Note that increasing the agitation rate from 'low' to 'high' (Figures 4 and 5) had less effect on conductivity distribution than did increasing the exit-hole size from 1 to 1.4 mm (Figures 5 and 6). Hence, it is likely that voidage fraction can be the main controlling variable in throwing power efficiency. Since most commercial electroplaters (and notably those involved in PCB manufacture) currently use a vigorous air agitation format, it may be the case that an alternative means of agitation could produce a 20–30% increase in conductivity and thus a net improvement in throwing power above the present levels. This argument is substantiated by the fact that when the conductivity probe was held in front of a pumped electrolyte flow (based on single phase fluid motion), only a 2% variation in conductivity was recorded, regardless of the flowrate or position. This could be another virtue of the pumped fluid eductor agitation systems when high throwing power is required.

The concept of low and high agitation rate is essentially relative because quantification involves not only flow but distribution and should be normalized with respect to the tank size. The presence or absence of jigged components in an industrial installation is a further difficulty to be considered.

3.2. *Conductivity as a function of voidage fraction*

The quantitative measure of agitation by air or a pumped solution is conventionally recorded in terms of the volume flow emerging from a hole or jet orifice. It is usual (and simplistic) to assume that agitation and flow rate are directly related, an assumption which holds unless the flow rate is extremely low or high. In the case

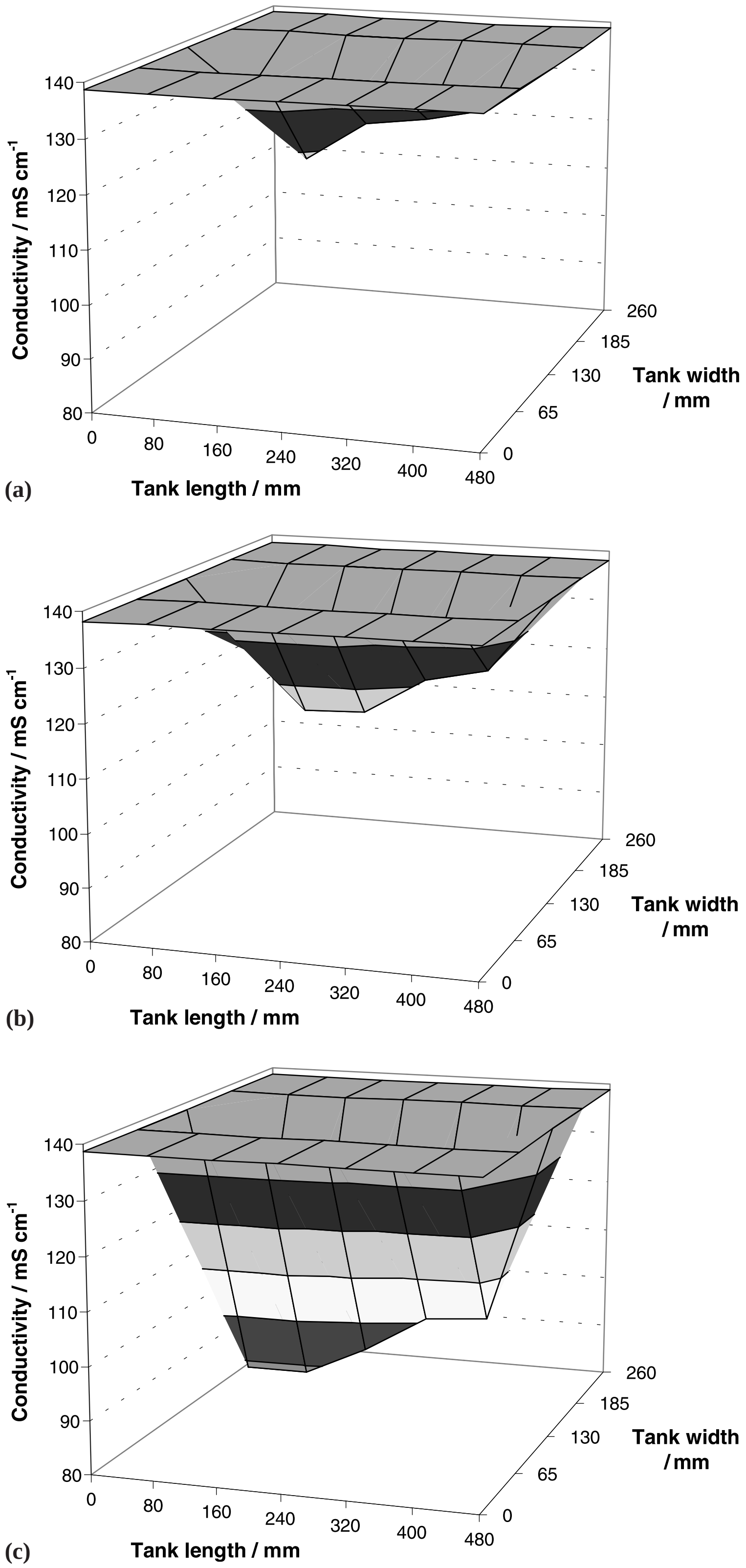

Fig. 2. Low agitation rate, single pump on l.h.s., 1 mm dia. sparge holes. (a) 165 mm plane (near electrolyte surface); (b) 110 mm plane (mid-depth); (c) 45 mm plane (at sparge pipe).

of a flow of air, the former will generate nonuniformity and the latter 'explosive' effects and air streaming rather than discrete bubble emission. Figure 7 shows that within the range considered to be suitable for electrode-position, the relationship was almost linear; each point represents an average of several measurements which was necessary to eliminate the local 'explosive-type' effects.

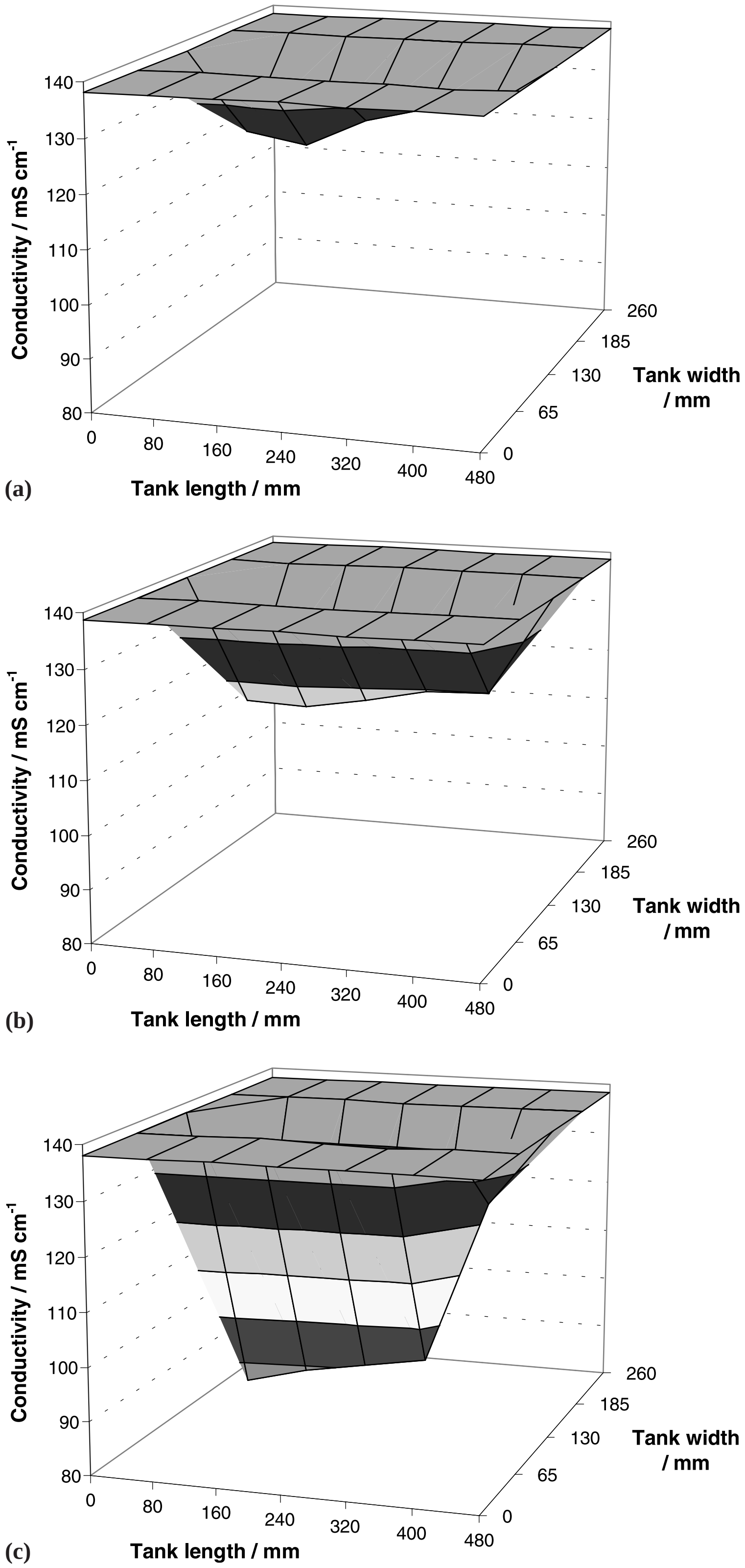

Fig. 3. High agitation rate, single pump on l.h.s., 1.4 mm dia. sparge holes. (a) 165 mm plane (near electrolyte surface); (b) 110 mm plane (mid-depth); (c) 45 mm plane (at sparge pipe).

The linearity of the graph shown in Figure 8 has in the past been of interest. Basically, the 'rule of mixtures' applies if uniform mixing occurs and hence this approach has been used in circumstances such as complete solution mixing (water and alcohol) or for determining particle distribution in a solid composite material. The limit of this analogy is reached by nonuniformity and directionality within the system. In

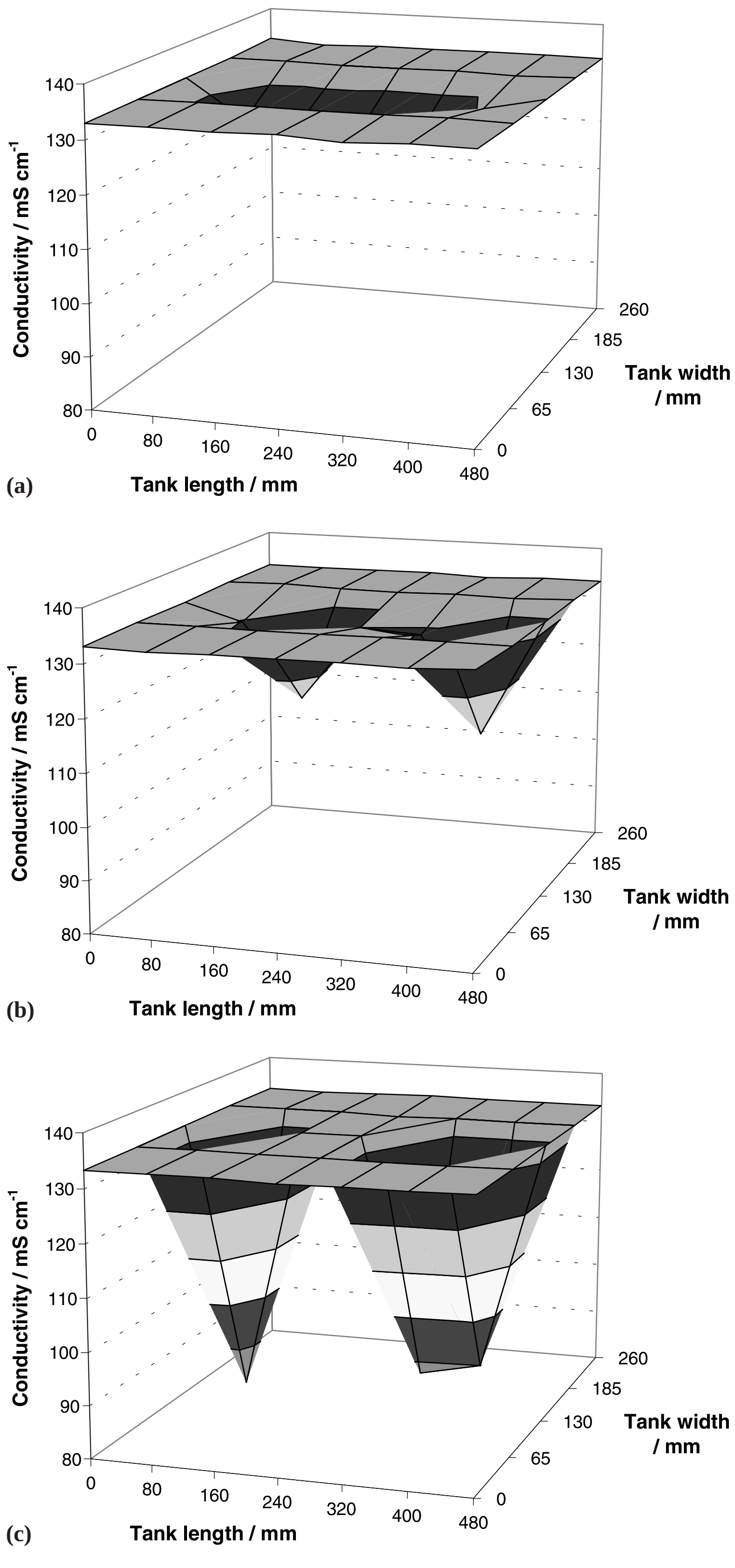

Fig. 4. Low agitation rate, dual pumps, 1 mm dia. sparge holes. (a) 165 mm plane (near electrolyte surface); (b) 110 mm plane (mid-depth); (c) 45 mm plane (at sparge pipe).

the context of air agitation, this means directional movement of bubbles and variability in shape and size, especially coalescence towards the top of a tank.

Turning to fluidisation or dispersion theory, other approaches have been invoked previously [11] and are summarized in Table 1. The relationship of concern is

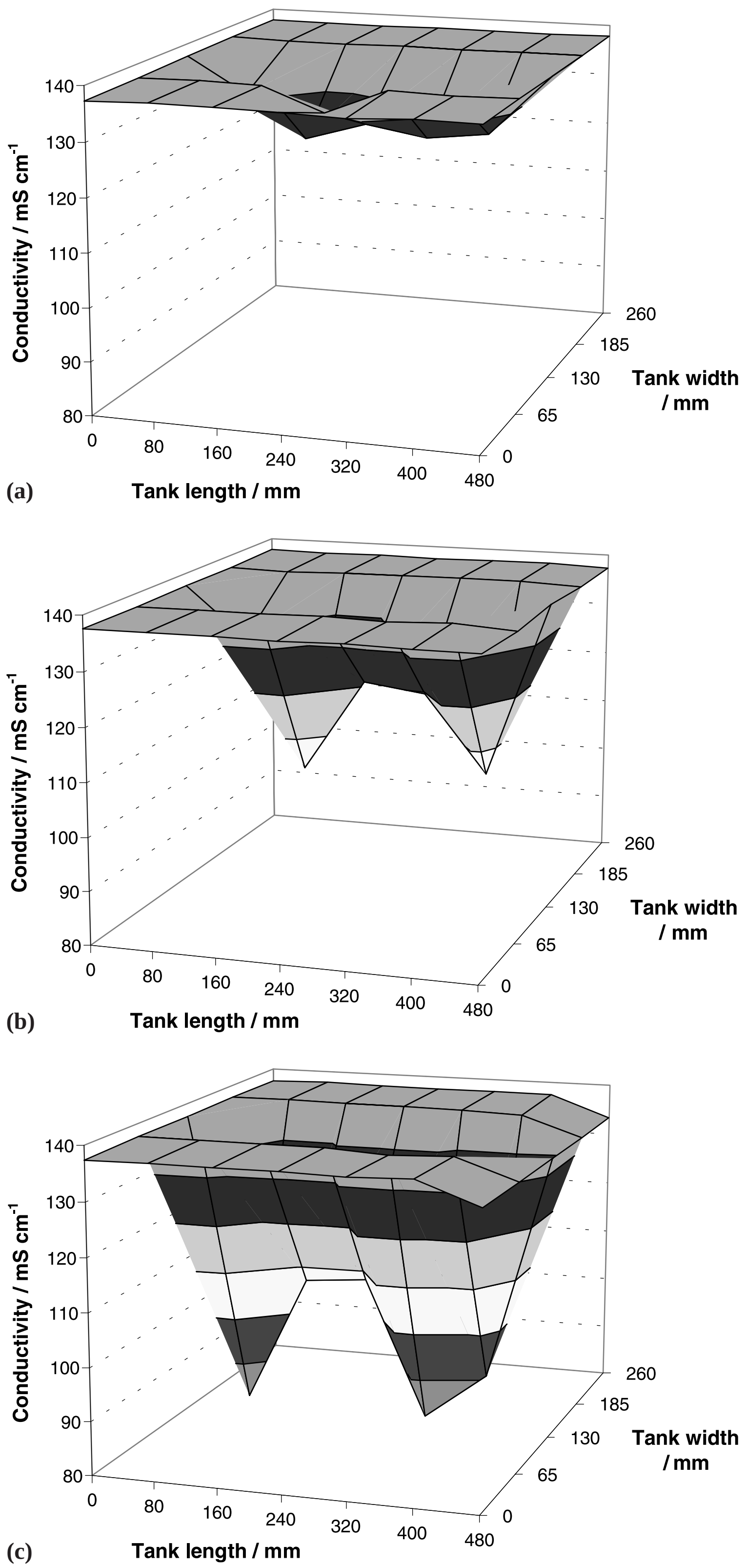

Fig. 5. High agitation rate, dual pumps, 1 mm dia. sparge holes. (a) 165 mm plane (near electrolyte surface); (b) 110 mm plane (mid-depth); (c) 45 mm plane (at sparge pipe).

between the *effective* conductivity of the two-phase fluid, κ as a fraction of the value for the unagitated solution, κ_0 and the gas voidage fraction, ε_g. There is no evidence that these alternative models offer better representation than the simple 'rule of mixtures' (Equations 1(a)–(c)) because over the agitation range shown in Figure 8, the loss of linearity must occur when the air fraction is above 0.2–0.25 where either coalescence inevitably takes place or individual emission at the sparge exit-hole never occurs. Our previous work has found that air fraction

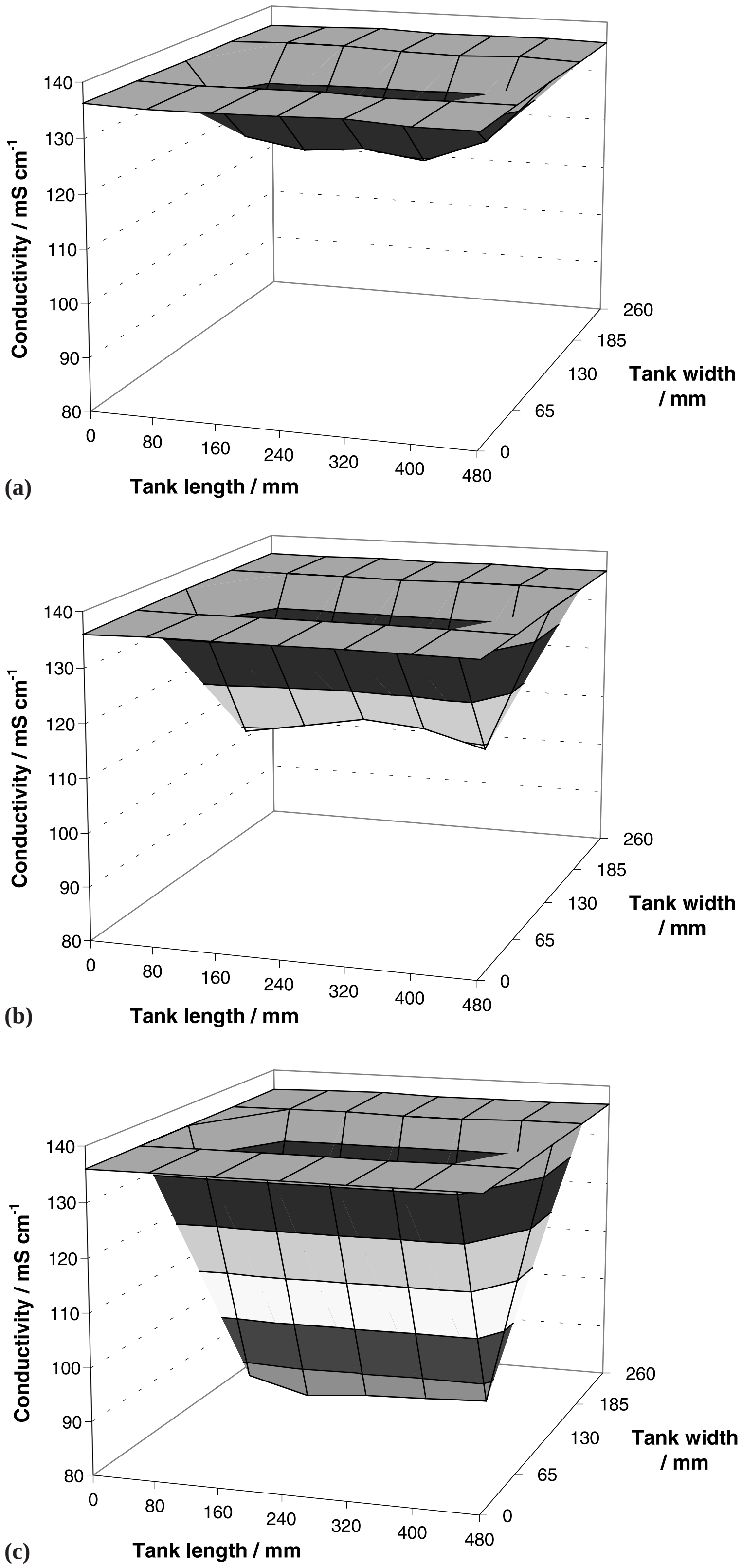

Fig. 6. High agitation rate, dual pumps, 1.4 mm dia. sparge holes. (a) 165 mm plane (near electrolyte surface); (b) 110 mm plane (mid-depth); (c) 45 mm plane (at sparge pipe).

remains linear with flow rate [4, 5] and earlier studies have shown that the differences between equations are small with the classical Maxwell–Rayleigh equation being as appropriate as any [12, 13]. There is now sufficient confidence in this approach for a resistivity sensor technique to be viable as a method of measuring air/liquid volume fractions in a turbulently stirred fluid [14]. While calibration of such a sensor is clearly vital,

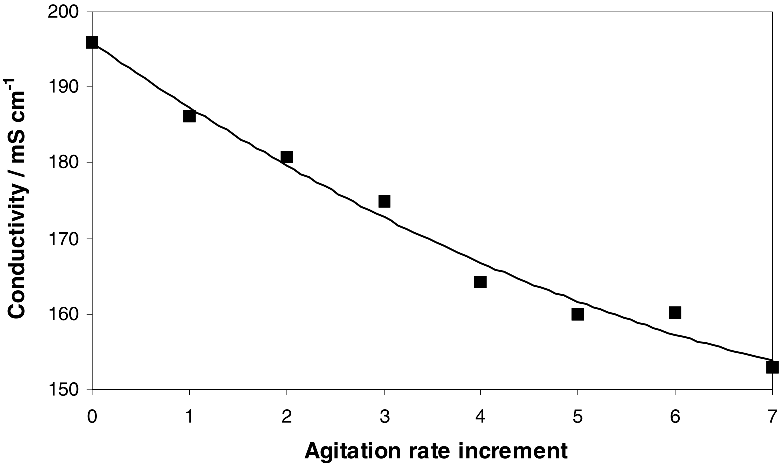

Fig. 7. Air agitation rate against conductivity in an acid copper solution (after [10]).

the various equations give surprisingly similar relationships (Figure 8) and hence the matter is not as critical as has been previously imagined.

3.3. *Throwing power considerations*

The Wagner number has often been used as an indicator of throwing power into recesses including through-holes and Equation 2 has shown that the relationship is direct. In the past various attempts have been made to optimise the through-hole uniformity by optimizing the Cu^{2+}/acid ratio [7, 8, 15]. If conditions for high speed deposition were required, the concentration of the H_2SO_4 would be increased in order to improve the support electrolyte effect and different polarization characteristics would be apparent. It should be recognized that variation in throwing power due to the influence of agitation on conductivity will depend primarily on the design of the air sparge system, rather than the nature of the surface and its recessing.

3.4. *Effects on electrolyte properties*

Air bubbles as a second phase will alter other physical properties of an electrolyte solution, including density and viscosity. Both can be predicted from the 'rule of mixtures' described for conductivity by Equation 1. However, these two properties will affect other deposition process parameters, typically those related to mass transport. For example, the Reynolds number (*Re*) is defined as

$$Re = \frac{\text{Inertia forces}}{\text{Viscous forces}} = \frac{u_{\infty}x}{\nu} \quad (3)$$

and the Schmidt number (*Sc*) as

$$Sc = \frac{\text{Momentum diffusivity}}{\text{Mass diffusivity}} = \frac{\nu}{D} \quad (4)$$

The implication is that a lower viscosity will lead to faster rates of deposition. Reducing electrolyte density

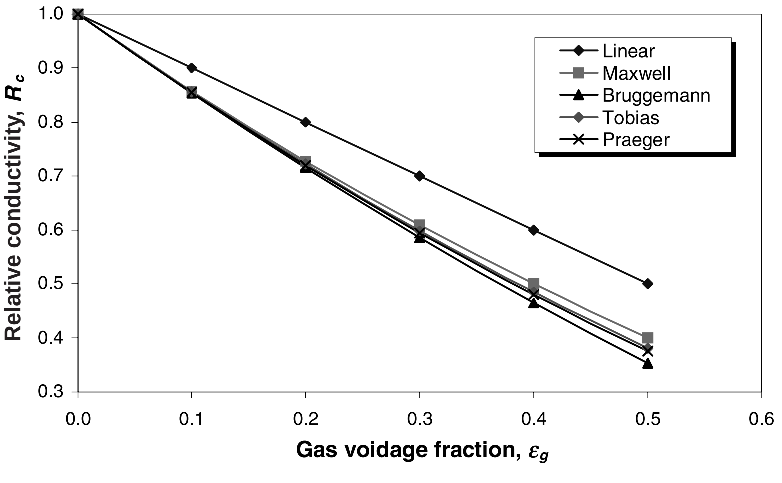

Fig. 8. Theoretical relationship between conductivity ratio and gas voidage fraction using equations in Table 1. Key: (◆) linear, (■) Maxwell, (▲) Bruggemann, (●) Tobias and (✖) Praeger.

Table 1. Equations for evaluation of relative conductivity ratio, R_C (after [11])

Name	Equation
Linear	$\frac{\kappa}{\kappa_0} = (1 - \varepsilon_g)$
Maxwell/Rayleigh	$\frac{\kappa}{\kappa_0} = \frac{(1 - \varepsilon_g)}{1 + (\varepsilon_g/2)}$
Tobias	$\frac{\kappa}{\kappa_0} = 8\frac{(2 - \varepsilon_g)(1 - \varepsilon_g)}{(4 + \varepsilon_g)(4 - \varepsilon_g)}$
Bruggemann	$\frac{\kappa}{\kappa_0} = (1 - \varepsilon_g)^{3/2}$
Praeger	$\frac{\kappa}{\kappa_0} = (1 - \varepsilon_g)(1 - \varepsilon_g/2)$

and viscosity may also yield lower fluid pumping power costs but this is essentially an energy economy issue; efficient bubble agitation will be of much greater significance to improving deposition rates at a cathode surface.

No account has been taken in this study of gas evolution at the cathode. In the case of the acid copper solution used, the effect is probably negligible because the cathode efficiency is high (>98%). However, there are solutions where the efficiency is much lower, the classical example being hexavalent chromium where it is below 30%. The fact that the gas is hydrogen and not air will have some bearing but this aspect is probably minor compared to the two-phase and electrode 'blanket' effects.

Surprisingly, there are no criteria used to define *quality* of air agitation in the terms discussed in this paper. The usual criteria are general observed uniformity of bubbling throughout the tank and improvement (albeit small) of deposition rates. Similarly, the specification of hole size in the sparge pipe is vague and nonquantitative in the context of flow rate and gas pressure; thus 1–2 mm hole diameter often suffices as a guide to standard practice. Although some further research work can be justified, action amongst plant designers is probably more useful at the present time.

4. Conclusions

Conductivity data have been obtained for a simple, model acid copper plating solution. It has been shown that with normal air agitation a loss of conductivity of 20–30% occurs. The loss is not uniform throughout the tank but is greatest at the bottom and least at the top. The implications for electrodeposition where good throwing power is required are related to the type and degree of agitation used. Estimating the degree of conductivity loss has been shown to closely follow a number of equations proposed by other researchers, the most convenient being the simple 'rule of mixtures' approach and the Maxwell–Rayleigh approach being more accurate when quantitative data, rather than a particular trend is required.

Acknowledgements

This research has developed out of a programme funded by the EPSRC and Lea Ronal (UK) Ltd under the CASE scheme. Thanks are due to Jeff Crosby and Keith Whitlaw (Lea Ronal) and also to David Bamford (Serfilco) for valuable discussions.

References

1. G. Guvendik and D.R. Gabe, *Trans. IMF* **77** (1998) 127.
2. G. Guvendik, C.J. Roberts and D.R. Gabe, *Plat. Surf. Finish.* **86** (1998) 44.
3. G.H. Kelsall and R. Menini, *IChemE* Symposium Series No. 145 (1999) 299.
4. S.A. Amadi, D.R. Gabe and M. Goodenough, *Trans. Inst. Met. Finish.* **72** (1994) 45, 66.
5. S.A. Amadi. PhD thesis, Loughborough University of Technology (1990).
6. M.R. Kalantary, D.R. Gabe and M. Goodenough, *Trans. Inst. Met. Finish.* **67** (1989) 24, 28.
7. M.R. Kalantary, D.R. Gabe and M. Goodenough, *J. Appl. Electrochem.* **23** (1993) 231.
8. M.R. Kalantary, PhD thesis, Loughborough University of Technology (1990).
9. M. Ward, D.R. Gabe and J.N. Crosby, *Trans. Inst. Met. Finish.* **76** (1998) 121.
10. G. Guvendik, MSc dissertation, Loughborough University (1997).
11. R.E. Meredith and C.W. Tobias, *Adv. Electrochem. Electrochem. Eng.* **2** (1962) 15.
12. R.E. de la Rue and C.W. Tobias, *J. Electrochem. Soc.* **106** (1959) 827.
13. L. Sigrist, O. Dossenbach and N. Ibl, *Int. J. Heat Mass Transf.* **22** (1979) 1393.
14. A.H. Castillejos and J.K. Brimacombe, *Met. Trans. B* **18** (1987) 659.
15. M. Goodenough and K.J. Whitlaw, *Trans. Inst. Met. Finish.* **67** (1989) 57.