Chemical Engineering Science

Volume 113, 3 July 2014, Pages 35–44

Effect of ultrasound on mass transfer during electro for electrodes separated by a narrow gap

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http://dx.doi.org/10.1016/j.ces.2014.03.026

Highlights

- Mass transfer during electrodeposition using side-on ultrasonic agitat
- Narrow electrode gaps and limitations of the limiting current technique
- Mass transfer correlation is developed for the side-on system for a nar
- Developed and fully turbulent flows were found for narrow and large ga
- Distortions in polarization data is caused by close placement of ultras

Abstract

This work reports an investigation on mass transfer by ultrasound agitatio electrodeposition on electrodes separated by a narrow inter-electrode ga experiments were performed to identify the mass transfer limiting current. current density was used to calculate mass transfer boundary layer thickn used to develop mass transfer correlations. Experiments were carried ou parallel copper discs which were positioned at gaps of 1, 0.5 and 0.15 cm between the ultrasonic probe and electrodes was varied between 3 and 1 polarisation data showed clear limiting current plateaux when the distance

electrodes was larger, however significant distortions were observed whe
0.15 cm. It was found that lower ultrasound powers of 9–18 W/cm^2 provide
agitation at narrower electrode gaps than powers exceeding 18 W/cm^2. S
correlations showed that in this system, developing turbulence occurs for l
electrode spacing, whereas for narrow electrode gaps fully turbulent corre
obtained. A 2-D current distribution model showed that potential distortio
observed in the polarisation data were caused by the close placement of
probe to the two parallel electrodes.

Keywords

Electrodeposition; Ultrasonic agitation; Enface Technique; Mass transfe
Limiting current

1. Introduction

Microfabrication has a variety of applications, including fabrication of ME
and micro-optic systems (Franssila, 2010 and Madou, 2012). The widesp
products has led to the search for new microfabrication processes (Dorai
2009, Samarasinghe et al., 2006, Whitaker et al., 2005 and Yu et al., 200
method is an electrochemical process, called EnFace (Roy, 2007). The p
selectively etch or plate metal at the microscale, using a patterned tool pla
proximity to the substrate surface, when a voltage or current is passed bet
Experimentally, it was shown that copper patterns ranging between 5 and
successfully etched (Schönenberger and Roy, 2005) or deposited (Wu et
vertical flow-by system.

Since the technique required inter-electrode gaps of less than 500 μm, fo
flow was needed to assist with species transport to and from the electrode
Furthermore, modelling studies showed that both forced convection flow v
electrode gap was a crucial parameter in controlling the ability of pattern t
and Roy, 2008 and Wu et al., 2011). Due to the issues associated with sc

cell, the ability to etch or plate at the microscale was also investigated usi
beaker-type geometry. However, implementing Enface in a non-agitated
restricted the mass transfer of ionic species within the inter-electrode gap
Roy, 2011). This investigation established that a method which directs ag
narrow gap was required.

It is well known that a diffusion layer forms at an electrode surface; if the re
out for short periods of time when diffusion is the dominant transport mech
classical equations developed by Cottrell (1903) and Sand (1901) may b
reaction results in a movement of ions in the bulk leading to natural convec
formation, then laminar or turbulent correlations for free convection, such a
(Wagner, 1949) and (1-b) (Fouad and Ibl, 1960) respectively, may be use

Alternatively, agitation can be provided via forced convection flow and co
Sherwood number correlations, such as Eq. (2) can be used (Tobias and

For the case of turbulent flow between two parallel plates the general Sher
correlation is

While these equations have been used extensively (Wragg, 1971 and Wr
1967), they are valid only when the two electrodes are sufficiently far from
interaction of boundary-layer takes place.

In fact, few mass transfer correlations exist for forced convection between electrodes are separated by a narrow gap. Although several studies on el growth (Kuhn and Argoul, 1995), surface adsorption (Texier et al., 1998) a (Compton et al., 1996b and Tolmachev et al., 1996) have been carried ou horizontal channel cell with a thin gap, this system has never been used fo electrodeposition purposes. Where steady state electrochemical deposi performed, it has been shown that electrochemical reactions within narro instabilities in material transport (Rosso et al., 2002 and Zelinsky and Pir example, silver deposition onto silver electrodes separated by a narrow g 0.01 M $AgClO_4$ electrolyte showed oscillations in the transfer of ions due t of boundary layers near the electrode surface (Zelinsky and Pirogov, 200 electrodeposition from 0.1 M $CuSO_4$ at parallel plates with an inter-electr 8 mm also exhibited concentration instabilities as the mass transport limi (Rosso et al., 2002). Both these studies confirmed that such thin gap cells electrodeposition due to mass transfer limitations.

Ultrasonics (US) is a forceful form of agitation which can improve stirring i systems (Compton et al., 1996a and Walton et al., 1995). An ultrasonic tra vibrating solid that can induce ultrasound waves through a solution which c cavitation. It is suggested that cavitation phenomena contributes to the en stirring (Compton et al., 1996a, Maisonhaute et al., 2001, Mason and Lori Ohsaka et al., 2010, Ramachandran and Saraswathi, 2009, Richardson e Walton et al., 1995 and Yeager and Hovorka, 1953). Much of the research established the improvement of mass transfer in electrodes which are far other (Compton et al., 1996a, Lorimer et al., 1996 and Marken et al., 199 and Saraswathi, 2009), but no information is available for cases where th gap between parallel plates.

The effect of US agitation has been most extensively studied by probes o to the working electrode surface (Compton et al., 1996a, Marken et al., 1996 and Ramachandran and Saraswathi, 2009), illustrated in Fig. 1(a). A

orientation, with a reduction of [redacted] at the working electrode for exar
demonstrated the importance of the distance from the probe tip to the cer
electrode surface (d_p), showing that the limiting current (i_{Lim}) is approxima
(Marken et al., 1996). This was attributed to the narrower jet of flow close t
compared to distances further away (Marken et al., 1996), thereby increas
of the mixing at the electrode surface as the tip is brought closer to it. The
power intensity on mass transfer has also been investigated (Compton et
Lorimer et al., 1996 and Ramachandran and Saraswathi, 2009). For insta
of a $K_4Fe(CN)_4$ redox reaction at a glassy carbon electrode, varying the p
showed that the diffusion layer thickness (δ) is approximately [redacted] (C
1996a). These investigations illustrated the importance of choosing appr
parameters to influence mass transfer in electrochemical systems.

Fig. 1.
US probe orientations relative to an electrode. (a) face-on; (b) side-on; and (c) side-on v
gap. Adapted from Marken et al. (1996).

To these authors' knowledge only one investigation has been carried out

ultrasound variables in the side-on geometry (Eklund et al., 1996), display
This investigation studied the effect of the 'side-on' probe on the mass tra
oxidation of ferrocene at a platinum plate electrode. The researchers deve
theoretical analysis based on earlier forced convection systems where the
the electrodes (Levich, 1962). They established that agitation conditions
using such a model, and that the diffusion layer across the surface of the e
uniform and had thicknesses of 10–12 μm at the downstream edge of the
et al., 1996).

At this point the effectiveness of US agitation to enable mass transport wi
plates, as illustrated in Fig. 1(c), has remained unexplored. In this work, we
to quantitatively assess the effect of US agitation on mass transfer during
metal deposition in a system with a combined geometry of a 'side-on' pro
inter-electrode gap. A well-established limiting current technique, widely u
determining material transport, is employed to determine the thickness of
boundary layers. The electrochemical system is copper deposition from a
$CuSO_4$ solutions, where flow instabilities have been encountered (Rosso
have measured the limiting current for copper deposition with and without
Limiting currents have been used to calculate the mass transfer boundary
and Sherwood number correlations have been developed. Experiments h
out using a small cell where parallel electrodes at gaps of 1, 0.5 and 0.15
placed. The gap between the US probe and electrodes has been varied b
1.5 cm. The usefulness of utilizing the limiting current method, which is ofte
determine mass transfer boundary layer thickness during electroplating, h
examined, particularly for the case of narrow electrode geometries.

2. Theory

It is suggested that the flow regime from an ultrasound probe tip is similar
flow from a pipe of the same diameter (Marken et al., 1996). Furthermore,
(1996) proposed that the flow of ultrasound waves over an electrode surfa
on' probe is analogous to flow over a plate. Based on this assumption, the

used an analysis proposed by Levich (1962) for forced convection. They c
describe the limiting current at an electrode when such a forced US agitat
a side-on arrangement (Eklund et al., 1996).

In Eq. (4), F, D, c_b and v are the Faraday constant, diffusion coefficient, bu
of reacting species and the kinematic viscosity respectively. The parame
the electrode, and the parameter x is the distance along the length of the e
edge closest to the probe. In Eq. (4) h_0 is the distance between the leadinç
momentum and the concentration boundary layers. The limits of the integr
and h_0+2r since the deposition reaction occurs at the metal surface (c.f. F

The only unknown parameter in the equation is U, the velocity of the flow fa
electrode surface. For US agitation, U is related to the ultrasound power a
solution velocity at a large distance from the plate. The effect of bringing th
is governed by changing the parameter 'd_p', which is defined as the distar
centre of the electrode to the US probe tip. It has been shown in earlier exp
distance between the probe and electrode of >3 cm is sufficiently far from
surface for Eq. (4) to hold (Compton et al., 1996a and Eklund et al., 1996)

Eklund et al. (1996) carried out experiments using a 20 kHz probe placed
34 mm away from a platinum plate electrode where ferrocene was oxidise
electrochemically. Experimentally measured limiting currents were used t
of U using Eq. (4) at various ultrasound intensities. This analysis showed t
proportional to US power, which is displayed in Fig. 2. This proved that 'flo
was a reasonable model for this side-on probe system.

Fig. 2.
A graph of *U* (best-fit value) obtained from the data (black square) published by Eklund
distance between the probe and the centre of the electrode was 34 mm.

3. Methodology

Experiments were carried out in a 500 ml cylindrical PVC cell with two pol
discs 1 cm in diameter acting as a cathode and anode, and faced each ot
an electrode gap (Fig. 3). The distance between the electrodes was altere
1 cm with the use of screw gauges on each electrode holder. The referenc
copper wire wrapped in PTFE tape with only the tip exposed, placed appr
from the cathode surface, above and to the side of the electrode gap. Cop
reference electrode in acidified $CuSO_4$ electrolytes, and has been used p
measurement of polarisation data (Meuleman and Roy, 2003 and Roy et
electrolyte solution used was an acidic electrolyte of 0.1 M $CuSO_4$+0.1 M

Fig. 3.
(a) Experimental set-up of the electrochemical cell used in this work with ultrasound pr
above the narrow electrode gap; (b) position of probe in solution above the working elec
variable parameter d_p. (c) Side view of placement of probe, with concentration (c) and fl
profiles demonstrating the development of the momentum and concentration boundary

An *Eco Chemie Autolab Potentiostat (PGSTAT30)* was used to apply lir
potential scans and *NOVA 1.7* software was used to input scan settings a
response data. The ultrasonic equipment used was a *SONICS Vibra-Cel
Processor* connected to a 20 kHz ultrasound probe with a 1.3 cm diamete
and was operated within a power range of 9–29 W/cm^2. The probe was p
gap in a side-on orientation (Fig. 3), with d_p=1.5–3 cm. The probe tip was
the solution by 0.4 cm for every probe–electrode distance.

The limiting current technique is based on the identification of limiting curr
standard electrode polarisation data. For any electrochemical reduction r
changes with potential, until it reaches the region where the reaction is ma
controlled. In this region the current becomes independent of the applied e
potential, and a current plateau is observed in the polarisation data. This v
termed as the mass transfer limiting current, is related to the diffusion laye
limiting current density can be used to calculate the diffusion layer thickne

$$i_{Lim} = \frac{zFD(c_b)}{\delta}$$

In Eq. (5), z is the charge on the reacting species, D is the diffusivity of the
and δ is the diffusion layer thickness. The value of δ was calculated using t
concentration stated in the experimental section and a diffusion coefficier
7.07×10^{-6} cm^2/s calculated using equations from Fenech and Tobias (19

The values of δ values calculated from the limiting current experiments we
develop Sherwood number correlations. *Sh* numbers were calculated by
$Sh=L/\delta$ where L is the characteristic length, in this case $2r$=1 cm, where r i

electrode (c.f. Fig. 8). The *Sc* number was calculated by $Sc=v/D$ where a k viscosity (v) of 1.004×10^{-2} cm^2/s was used and the diffusivity (D) was the used in the limiting current calculations. The value of *Re* was based on the diameter (d_H), which was used to calculate the equivalent diameter (d_e). T procedure is stated in the Appendix.

4. Results

Fig. 4a–c show the linear polarization scans for copper deposition at the using US agitation. Limiting current plateaux are observed as expected d deposition, although the data for lower probe–electrode distances and na gaps exhibit smaller plateaux regions, resulting in a difficulty in measurem current density (i_{Lim}). This measurement was also made more difficult due fluctuations caused by cavitation bubble oscillations and micro-jetting res current peaks, which have been previously observed in side-on (Eklund et as face-on (Compton et al., 1996a and Marken et al., 1996) and probe ar 4b and c, where probe–electrode distance or inter-electrode gap are sma hydrogen discharge potentials apparently occur at lower potentials, which of limiting current difficult.

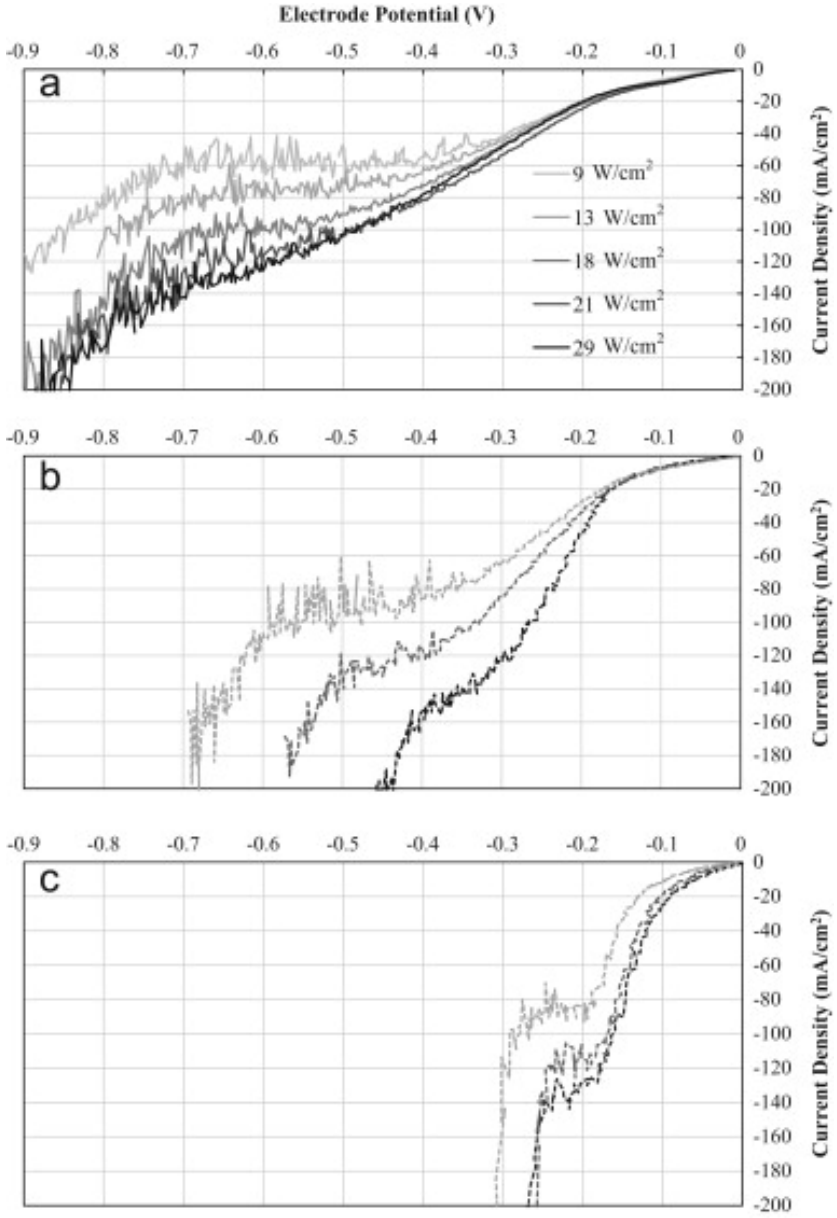

Fig. 4.

Linear Potential scans with a 0.1 M $CuSO_4$+0.1 M H_2SO_4 electrolyte; Scan Rate=5 m ultrasound intensities (9–29 W/cm^2), h_e=1 cm; d_p=3 cm. (b) h_e=0.5 cm; at varying d_p (grey), 2 cm (dashed grey) and 1.5 cm (dashed black) at fixed p of 18 W/cm^2. (c) h_e=0. ultrasound conditions as for 'b' and varying d_p at distances of 3 cm (dashed light grey), and 1.5 cm (dashed black).

The values of i_{Lim} for an inter-electrode gap of 1 cm (Fig. 4a) are in the rar
−130 mA/cm^2. This value is significantly greater than the i_{Lim} value measu
under silent conditions, which was recorded at −10.5 mA/cm^2 respectivel
agitation provided by ultrasound significantly increases the rate of mass t
ions towards the substrate. This enhancement in limiting current density w
intensity has been previously reported in sonoelectrochemical investigati
(Eklund et al., 1996) and face-on geometry (Compton et al., 1996a and R
and Saraswathi, 2009).

Fig. 4b displays linear potential scans under ultrasound conditions for a na
electrode gap and varying probe–electrode distances. The value of i_{Lim} a
electrode gap of 0.5 cm is approximately 90, 122 and 140 mA/cm^2 for the
distances of 3, 2 and 1.5 cm respectively illustrating the increase in mass
probe is brought closer towards the electrode, evident in previous ultraso
where the probe–electrode distance is varied (Compton et al., 1996a an
1996; Ramachandran and Saraswathi, 2009). It is suggested that this is c
presence of a higher flow velocity at shorter distances from the probe tip (
1996).

Fig. 4c displays linear potential scans under ultrasound conditions for an e
inter-electrode gap and varying probe–electrode distances. The value of
virtually unchanged when the electrode spacing is decreased from 0.5 to
demonstrating that ultrasound is an effective form of agitation even for nar
gaps. However, the polarisation data are significantly different when using
gap, i.e. 0.15 cm, being distorted, with a very small plateaux region.

The i_{Lim} values from polarization data were used with Eq. (4) to calculate t
thickness of the diffusion layer (δ) at the cathode at varying US powers an
distances of 1 cm (large) and 0.15 cm (small), displayed in Fig. 5. These v
layer thickness are calculated for a probe–electrode distance of 3 cm, wh

deemed to be sufficiently far from the electrode surface.

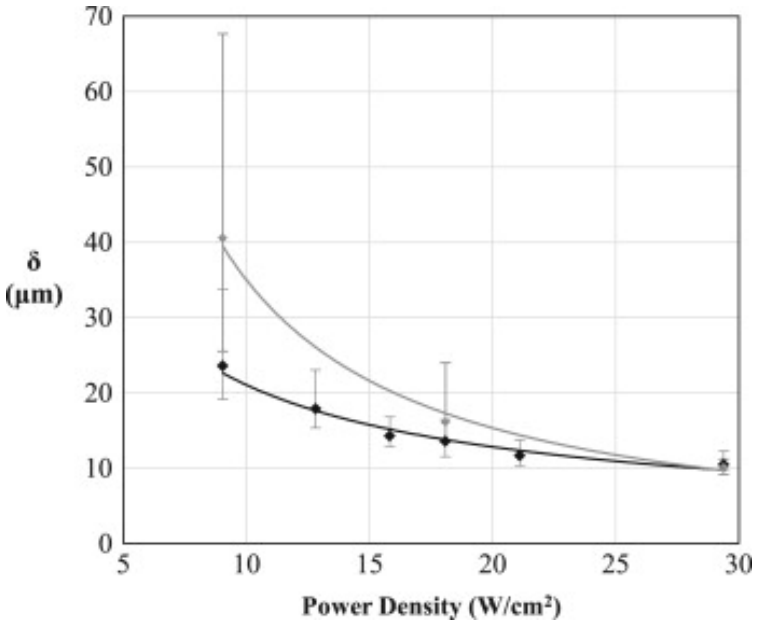

Fig. 5.
Diffusion layer thickness (δ) calculated using experimental limiting currents and Eq. (5
power density. h_e=0.15 cm (grey), 1 cm (black); d_p=3 cm.

As expected, the boundary layer is larger at lower US intensities compare
intensities for the case for the constant electrode separation of 1 cm. Narr
electrode gap from 1 cm to 0.15 cm increases the δ due to constriction of
Interestingly, the decrease in the thickness of the boundary layer for the sy
narrower gap is higher, as is seen from the data at US intensities higher th
Finally, for both electrode gaps, a minimum diffusion layer thickness (δ_{min}
reached as the ultrasound power is raised. It has been suggested that this
the limiting conversion of ultrasound energy to turbulent liquid flow (Marke
all cases shown in Fig. 4a–c, the values of δ achieved with US are more th
under silent conditions, which shows the usefulness of such agitation.

In order to examine more deeply into the mechanism of US agitation at the surface, Sherwood number correlations were developed. For this purpos velocity, U, far away from the electrode is required. The flow velocity (U) o ultrasound waves flowing between the electrodes at different ultrasound p was estimated using the relationship formulated by Eklund et al. (1996), w Fig. 2. The value of Reynolds number, Re, was calculated using $Re=(Ud_H$ of U shown in Fig. 2. The Re numbers for the range of ultrasound powers e experiments were found to be approximately 700–2000 and 2700–7400 large gaps, respectively, as shown in Table 2 in Appendix.

Table 1.
Calculated change in potential at the cathode surface for varying electrode gaps and pr

Change in probe distance, d_p (cm)	Change in electrode gap, h_e (cm)	Change in po cathode (V)
3–1.5	1 (constant)	+0.130
3–1.5	0.15 (constant)	+0.085
3 (constant)	1–0.15	+0.135
1.5 (constant)	1–0.15	+0.090
3 to 1.5	1–0.15	+0.220

Sherwood–Schmidt–Reynolds numbers correlations for copper depositi for electrode gaps of 0.15 cm and 1 cm, shown in Fig. 6. The line of best-fi correlations displayed in Eqs. (6) and (7) for electrode gaps of 1 cm and 0 respectively.

$$Sh = 1.7 \times 10^{-3}\left(Re\, Sc \frac{d_e}{L}\right)^{0.82}$$

$$Sh = 9 \times 10^{-6}\left(Re\, Sc \frac{d_e}{L}\right)^{1.38}$$

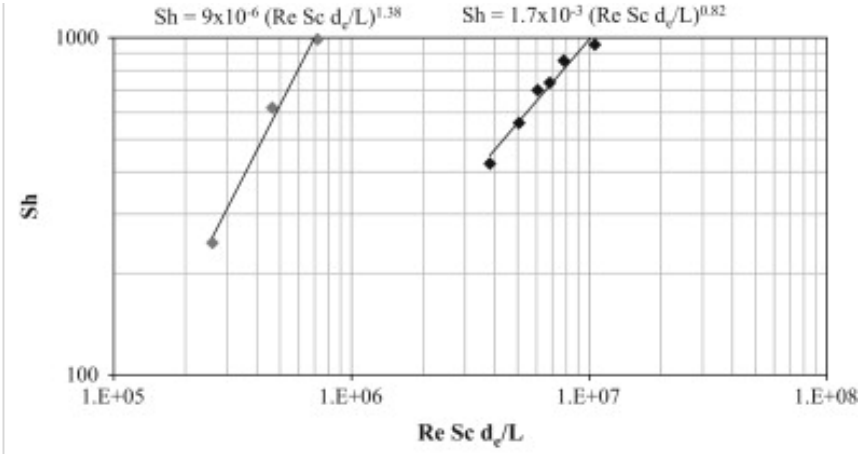

Fig. 6.
Mass transfer correlations using US agitation. Data shown for US power 18 W/cm^2 and distance of 3 cm, where the US source is far away from the electrode. Inter-electrode g (grey) and 1 cm (black).

These correlations can be compared against standard mass transfer cor for forced convection flow between two parallel electrodes, displayed in E *b* for the 1 cm electrode gap is ~0.8, showing the onset of turbulent flow. H turbulent flow becomes fully developed when the electrode gap is narrowe illustrated by the value of *b* of ~1.4 in Eq. (7). It is suggested that this is pos formation of eddies at the top of the narrower gap, which could occur whe of ultrasound waves come into contact with the top section of the electrod

It is significant that the *Sh* correlation shows fully developed turbulence for which means that the efficacy of US is higher even though the *Re* values a example, at 29 W/cm^2, the *Re* for the small and large gap is 2000 and 74(but the value of δ is virtually the same. The turbulence in the narrower gap the interaction between the US waves and the edges of the parallel electr eddy formation, which needs to be investigated further.

5. Discussion

A noticeable issue in this work was the difficulty in detecting a limiting curr
the electrodes were placed close to each other or when the distance betw
electrode was lowered. Although current oscillations have been observed
investigations (Compton et al., 1996a, Eklund et al., 1996 and Marken et
both side-on and face-on geometries, there is less information on distorti
data during electrochemical reactions. Marken and Compton (1996) have
current can flow to the US probe itself, since it is metallic, and has also sug
of obviating this problem; including bipotentiostatic control and electrically
probe. However, bipotentiostats are not used in industry and therefore ca
applications, and electrically insulting the probe may lower the ultrasound
Polarisation data of other researchers have also shown that limiting curre
observed during US agitation (Reisse et al., 1994). In our case, it can be s
that the plateaux region is very small. This means that the limiting current t
have only limited applicability for measuring mass transfer limitations for e
systems using US.

In order to examine more deeply into the apparent distortion in potential m
further analysis was carried out. There is a possibility that the probe is acti
relative to the electrodes. However, Marken and Compton (1996) sugges
ultrasound probe placed within an electrolyte solution of an electrochemic
second working electrode; therefore the surface of the probe was modelle
cathode. A primary current distribution model of copper electrodepositior
using a commercial electrodeposition software, ElSyca (ElSy, SA) using
model of the cell in Fig. 3. The software was used to determine if the poter
hydrogen evolution region begins could shift from −0.6 V to −0.3 V as the
decreased from 0.5 to 0.15 cm at a probe distance of 3 cm, as was obser
polarisation experiment shown in Fig. 4.

The calculation used for the model assumed that there is a uniform concer
ions in the solution and also constant electrolyte conductivity. The well-knc
the flux of an ionic species k (N_k) was used, shown in Eq. (8).

$$N_k = -D_k \nabla c_k + c_k v - z_k u_k F c_k \nabla \phi$$

where u_k is the mobility of species k ($cm^2 mol/J\ s$) and $\nabla\phi$ is the potenti
The accumulation of species k can be expressed as the equation showr

$$\frac{\partial c_k}{\partial t} = -\nabla \cdot N_k + R_k$$

where R_k is the production rate of species k (mol/s). A more convenient
equation can be written as Eq. (10), derived by substituting Eq. (8) into E

$$\frac{\partial c_k}{\partial t} + v \cdot \nabla c_k = z_k F \nabla (u_k c_k \nabla \phi) + \nabla (D_k \nabla c_k), \quad k = 1 \ldots n$$

The velocity of an incompressible fluid flow in electrochemical systems is
well-known Navier–Stokes equation, with constant density and viscosity

$$\nabla \quad v = 0$$

The electric potential (Φ) in an electrochemical system can be expressed
equation, shown in Eq. (12). However, this can be replaced with the electr
expression in Eq. (13) due to the condition that the bulk electrolyte solutior
neutral.

where ϵ is the dielectric constant of the solution (Farad/m). The current c
be described by Eq. (14). If N_k is substituted by Eq. (8), then the current
expressed in terms of diffusion, convection and migration. If the conducti
into account (Eq. (13)), along with the condition of electroneutrality (Eq. (
current density can be given by Eq. (16).

For steady-state conditions, Eq. (10) can be omitted. If there is a continuo
solution, it can be assumed that convection is dominant and concentratior
omitted, therefore Eq. (10) can be simplified to Eq. (17), the well-known L
This means that the current density can be expressed as Eq. (18).

$$\sigma\nabla^2\phi=0$$

$$i=-\sigma\nabla\phi$$

This model is solved using the Boundary Element Method in ElSyca, using
conditions that the current density at each point at the insulating walls of th
surface of the solution is zero. This means that the current flows to the elec
case the anode, cathode as well as the US probe placed in solution

where *y* denotes the normal distance from the surface.

A constant temperature of 293 K was used and the electrolyte conductivity
59.8 mS/cm. The dimensions of the US probe were modelled as a rectan
and of height 1.3 cm, 0.4 cm respectively, placed above the electrode gap
were used on both the cathode and anode, 120 elements on the surface o
the electrodes and 30 elements on the side of the probe. The convergenc
density calculation was achieved when the current residual reached a valu
<0.001 mA/cm^2 and the calculation was completed within 6 iterations (at r
of iterations of 20).

Typical results from the modelling analysis are presented in Fig. 7. The pc

electrode gaps of 1 cm and 0.15 cm with the ultrasound probe at probe–e
distances of 3 cm and 1.5 cm are shown in the figure. The results show tha
presence of a large metallic probe, significant distortion in the potential fie
electrodes are brought closer together or when the probe is brought close
electrodes the distortion in the field is greater and current begins to flow to
proposed by Marken and Compton (1996). This resulted in copper depos
surface, observed during our polarization experiments. The current flow fr
anode to the probe surface meant that smaller current densities were calc
section of the cathode surface in the modelling. This would therefore be th
deposit thickness non-uniformity along the cathode length.

Fig. 7.
Potential isolines within the electrochemical cell with an ultrasound probe placed in the
with cathode (left) and anode (right). Potential applied=−0.1 V. (a) h_e=1 cm; d_p=3 cm. (
d_p=1.5 cm.

The change in potential at the cathode at different probe distances and el
displayed in Table 1. Interestingly, the cathode potential can shift by 0.085
positive direction depending on the proximity of the US probe and the two
electrodes. This shift in potential is of a similar magnitude to the shift in po
experimentally in Fig. 4, which explains the differences in polarisation dat
different electrode geometries. Both narrowing the electrode gap and low
result in potential distortions which shorten the current plateaux, and also
flow through the probe. This measured limiting current is therefore inaccur
the distance between the probe and the electrodes. Our modelling data sl
the total current flowed to the probe for the smallest probe to electrode dis
findings therefore show that within very constricted geometries, the emplo
limiting current technique may be limited.

Table 2.
Calculated Reynolds numbers at varying powers for two difference electrode gaps, with
power, obtained from Fig. 2.

Electrode gap (cm)	Power (W/cm^2)	Velocity, U(cm/s)	Re
1	9	27	2686
	18	48	4795
	29	75	7430
0.15	9	27	701
	18	48	1251
	29	75	1938

6. Conclusions

The effect of a side-on ultrasound probe on the mass transfer during copp

narrow inter-electrode gaps was investigated. The limiting current technic determine the diffusion layer thickness, which were then used to determin correlations. It was found that ultrasonic agitation significantly improved m the ability to increase limiting currents by a factor of 10.

Ultrasound powers of 9–18 W/cm^2 were found to provide more effective a expected, stirring at the electrode surface increased as the US probe was closer proximity to the electrodes. Sherwood correlations showed that turb present near the electrode surface when a side-on probe is used. For larg spacing the developing turbulence was observed, whereas for narrow ele turbulent correlations were obtained.

Polarisation data for copper deposition were found to be distorted when t probe was brought closer to the electrodes, and when the anode and cath proximity. A current distribution analysis showed that the distortion in pola caused by the close placement of the metallic US probe to the two paralle These findings hold implications for limiting current analyses used to study within narrow electrode gaps in a horizontal regime or within concentric cy electrodes in close proximity to each other (Coeuret and Legrand, 1981), other ultrasonic applications where the source of ultrasound has to be plac proximity to a substrate or work piece.

Nomenclature

Φ	potential (V)
a	constant coefficient in Sherwood correlation
A	cross-sectional area of channel between the electrodes (cm^2
b	exponent in Sherwood correlation
c	concentration (mol/cm^3)
d	distance (cm)

D	diffusivity (cm^2/s)
δ	diffusion layer thickness (cm)
h_e	electrode gap (cm)
ϵ	dielectric constant of the solution (Farad/m)
F	Faraday constant (96485 A s/mol)
Gr	Grashof Number (dimensionless)
h_0	distance between the leading edge of the momentum and the boundary layers (cm)
i	current density (mA/cm^2)
I	current (mA)
L	characteristic length (cm)
N	flux of species (mol/cm^2s)
v	kinematic viscosity (cm^2/s)
p	ultrasound power intensity (W/cm^2)
σ	conductivity (S/m)
r	radius (cm)
Re	Reynolds Number, dimensionless
R	production rate (mol/s)
Sc	Schmidt number, dimensionless
Sh	Sherwood number, dimensionless
t	time (s)
U	limiting solution velocity at a larger distance from the plate (cm

u	mechanical mobility of species k ($cm^2 mol/J.s$)
w	electrode width (cm)
x	length along the electrode from the edge closest to the probe (
z	charge of species

Subscripts

b	bulk
e	equivalent (diameter) (cm)
H	hydraulic (diameter) (cm)
k	species
Lim	Limiting
min	minimum
p	distance from probe tip to the centre of the electrode surface (
$sono$	in the presence of ultrasonic agitation

Acknowledgements

Simon Coleman acknowledges the studentship support by EPSRC, UK g
EP/J500288/1. This work was supported by EU “MESMOPROC” Grant 3
Chemical Engineering workshop is acknowledged for cell fabrication.

Appendix

Reynolds number calculations

The electrode dimensions were simplified to 1 cm square electrodes for t
analysis, shown in the schematic in Fig. 8. The hydraulic diameter (d_H) wa

the equation $d_H=4A/(4r+2h_e)$, where A is the cross-sectional area of the c
the electrodes, r is the radius of the electrode and h_e is the electrode gap.

Fig. 8.
Schematic of electrode gap for calculation of d_H with assumption of square electrodes.
length, A=cross-sectional area, h_e=electrode gap.

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