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Comparative analysis of mass transfer at vibrating electrodes

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The application of oscillatory flows to electrochemical processes was found to increase the rate of mass transfer and improve the quality of deposit. Various mechanisms to which this phenomenon is attributable are discussed and expressions for the average rate of mass transfer, resulting thereof, are derived.

Comparison with experimental data indicates that the stretched-film concept, although an oversimplification of the physical situation, is most successful in correlating the data.

Nomenclature

A = Amplitude of oscillatory motion (cm)
c = Concentration of the diffusing species (g mol cm^{-3})
D = Diffusivity (cm^2 s^{-1})
F = Frequency of oscillation (Hz)
k = Instantaneous mass transfer coefficient (cm s^{-1})
$\bar{k}_{\text{vib}}$ = Time-average vibratory mass transfer coefficient (cm s^{-1})
L = Length of active area (cm)
S = Velocity gradient at solid–liquid interface (cm s^{-1} cm^{-1})
u = Oscillatory velocity of fluid layers adjacent to the electrode (cm s^{-1})
u_{Rel} = Relative velocity between the electrode and the bulk of the fluid (cm s^{-1})
v = Relative velocity between the electrode and the fluid layers adjacent to it (cm s^{-1})
W = Width of active area (cm)
x = Distance along the surface of the electrode (cm)
z = Distance perpendicular to the surface of the electrode (cm)
ξ = Dimensionless distance = $z(S/9Dx)^{1/3}$
η = Dimensionless distance = $\omega z^2/2\nu$
ν = Kinematic viscosity of the electroyte (cm^2 s^{-1})
ω = Angular frequency = $2\pi F$

1. Introduction

In recent years, there has been a growing interest in the application of oscillatory flows to electrochemical processes. This has been prompted by the improvement, in both the rate of deposition and quality of deposit, resulting when the electrode is vibrated or when the electrolyte is subjected to sonic and ultrasonic waves.

The utilization of oscillatory flows was found to reduce concentration polarization with the consequent acceleration of metal deposition and dissolution rates [1–5]. It was also found to increase metal deposition current efficiency [6], facilitate electrode passivation and gas liberation [7–9], and the resultant deposit is reportedly brighter, harder, less porous and usually of a finer grain size [10–13]. Metal corrosion [14–16], production of metal powders [17, 18], and electrochemical machining [19], are also enhanced by the application of oscillatory flows.

Literature on the application of ultrasonic energy in electrochemical processes is extensive and has been the subject of recent reviews [20, 21], but controversy still exists over the precise effect which ultrasound has, and the factors responsible for the previously mentioned beneficial effects. This is probably due to the fact that the geometry of the plating baths, and the method by which ultrasound is applied to the electrolyte, affect the efficiency with which energy is transmitted to the region near the electrodes. On the other hand, none of these difficulties are encountered with systems in which the electrode is vibrated and these could thus be used to gain a basic understanding of the mechanism responsible for mass transfer enhancement in oscillatory flows. Furthermore, by vibrating the electrode instead of the electrolyte the energy requirements are greatly reduced while retaining most of the advantages obtained from ultrasonic agitation. This arises from the need to oscillate only the thin layer adjacent to the electrode rather than the whole electrolyte, as would be the case when ultrasonic waves are applied to the bath.

The aim of this paper is to present various mechanisms by which enhanced transfer rates at vibrating electrodes could be explained, and to compare these with recently obtained experimental data.

2. Mechanisms for mass transfer enhancement at vibrating electrodes

Many mechanisms have been proposed to account for the increased average transfer rates obtainable when an oscillatory motion is generated between fluids and solid surfaces. These include quasi steady-state models [22, 23], the stretched-film concept [14, 24, 25], reduced boundary layer thickness [1, 14, 26] and analyses that take into consideration the combined effect of the oscillating velocity and concentration fields [27, 28].

The simplest of these mechanisms is the quasi steady-state model which assumes that at any instant, steady-state conditions corresponding to the instantaneous velocity are achieved. This mechanism is expected to be valid when the frequency of the oscillatory motion is low and its amplitude is large relative to the characteristic dimension of the solid surface.

The average rate of mass transfer resulting from fully developed flow over flat plates is given by [29]

$$k = \sqrt{\left(\frac{4D}{\pi L}\, u_{\mathrm{Rel}}^{0\cdot5}\right)}\,. \tag{1}$$

At high vibration intensities, natural convection has only a small effect on the velocity field; the relative velocity between a sinusoidally vibrating plate and the bulk of the electrolyte will then be given by

$$u_{\mathrm{Rel}} = A\omega \cos \omega t \tag{2}$$

Consequently, when the quasi steady-state prevails the average rate of mass transfer is given by

$$\begin{aligned} \bar{k}_{\mathrm{Vib}} &= \sqrt{\frac{4D}{\pi L}}\left[\frac{2\omega}{\pi}\int_0^{\pi/2\omega} (A\omega \cos \omega t)^{0\cdot5}\,\mathrm{d}t\right], \\ &= 0{\cdot}85\sqrt{(A\omega D/L)}. \end{aligned} \tag{3}$$

The stretched-film concept was successfully used to correlate the data of many vibrating systems [14, 24, 25]. It attributes the enhanced transfer coefficients, resulting from the vibration of solid surfaces at high frequencies and small amplitudes, to the formation of a film of the diffusing species. The area of this film corresponds to the total area swept out during each period and is thus larger than the active area at the solid–liquid interface. Because of the high frequency and slow rate of diffusion, the concentration along this stretched film is assumed to be equal to that existing at the interface.

Applying this concept to a vibrating flat surface having an active area of width W and length L, the stretched film will have an effective area of

$$\text{Effective stretched-film area} = W(L + 2A). \tag{4}$$

Using this effective area and a Reynolds number based on the average oscillatory velocity $4AF$, the average rate of mass transfer at vibratory surfaces becomes [29]

$$E = \frac{\bar{k}_{\mathrm{Vib}}}{\bar{k}_{\mathrm{steady}}} = 1 + K\frac{A\omega L}{\nu}\left(1 + \frac{2A}{L}\right)^2 \tag{5}$$

where K is an empirically determined consta

Using the analogy between mass and mome tum transfer, Krasuk and Smith [30] investigat the influence of pulsations on the rate of mass transfer. They were able to analyse the situation where pulsation intensity is small relative to the steady flow. Good agreement between theory and experimental data was obtained but scatter increased with increasing vibrational intensity-ratio. Their analysis is therefore inapplicable to vibrating electrodes where the mean flow due to natural convection is usually much smaller than the vibrational velocity.

On the other hand, the analogy between mass and momentum transfer leads to the assumption that vibrational parameters will affect the diffusion boundary layer in a manner similar to that of the hydrodynamic boundary layer. The thickness of the latter is reduced by the application of vibration and is proportional to $\surd(\nu/\omega)$ [31]. Consequently, if mass transfer enhancement at vibrating surfaces results from the thinning of the boundary layer (as was assumed to be the case [1, 14]) its value would be given by

$$\bar{k}_{\mathrm{Vib}} \propto \surd(\nu/\omega) = K'\surd(\nu/\omega). \qquad (6)$$

Some analyses took into consideration both the oscillating velocity- and concentration-fields. This approach was adopted to explain mass transfer enhancement in pulsating flow [27] and to correct the response of electrochemical transfer probes to turbulent fluctuation [28]. The presence of a relatively large steady-stream complicated the situation and analytic expressions were obtained only for the limiting cases of very high and very low frequencies. The following analysis, which is close to that suggested by Lombardi and Krasuk [32], does not suffer from these limitations.

When a flat plate is oscillated sinusoidally in a still fluid, its velocity is given by

$$u_{\mathrm{wall}} = A\omega \cos \omega t. \qquad (7)$$

The fluid layers adjacent to the plate are also set into an oscillatory motion whose velocity is [25],

$$u(z, t) = A\omega\, \mathrm{e}^{-\eta} \cos(\omega t - \eta), \qquad (8)$$

where

$$\eta = \surd(\omega z^2/2\nu). \qquad (9)$$

The relative oscillatory velocity between the vibrating flat electrode and the layers adjacent to it is thus given by

$$v(z, t) = A\omega[\mathrm{e}^{-\eta} \cos(\omega t - \eta) - \cos \omega t]. \qquad (10)$$

Considering a rectangular transfer area on the surface of the electrode, whose length is L and width W, the continuity equation becomes

$$v\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial z^2}, \qquad (11)$$

with the boundary conditions,

$$\left.\begin{array}{lll} \text{(I)} & c = c_{\mathrm{Bulk}} & \text{at } z = \infty \\ \text{(II)} & c = 0 & \text{at } z = 0, \text{ and } 0 < x < L \\ \text{(III)} & c = 0 & \text{at } z = 0, \text{ and } 0 > x > L \end{array}\right\}. \qquad (12)$$

Electrolytes usually have large Schmidt numbers, for which case the thickness of the concentration boundary layer is much smaller than the momentum boundary layer. The velocity near the solid–liquid interface can thus be linearized as

$$v = Sz \qquad (13)$$

where S is the velocity gradient at the interface given by

$$S = \left.\frac{\partial v}{\partial z}\right|_{z=0} = \frac{A\omega^{3/2}}{\nu^{1/2}} \cos\left(\omega t + \frac{\pi}{4}\right). \qquad (14)$$

Using Equation (13) and the dimensionless variable $\xi = z(S/9Dx)^{1/3}$, the continuity equation can be solved for boundary conditions (12) yielding

$$\frac{c}{c_{\mathrm{Bulk}}} = -\frac{1}{0{\cdot}893}\int_0^{\xi} \mathrm{e}^{-\xi^3}\, \mathrm{d}\xi. \qquad (15)$$

The instantaneous value of the local mass-transfer coefficient could then be evaluated from

$$k_{\mathrm{Vib}}(x, t) = -\frac{D}{c_{\mathrm{Bulk}}}\left.\frac{\partial c}{\partial z}\right|_{z=0}, \\ = \frac{D}{0{\cdot}893}\left[\frac{S}{9Dx}\right]^{1/3} \qquad (16)$$

and the surface-average mass-transfer coefficient thus becomes

$$k_{\mathrm{Vib}}(t) = \frac{D}{0{\cdot}893}\left[\frac{S}{9D}\right]^{1/3}\int_0^L x^{-1/3}\, \mathrm{d}x \\ = \frac{0{\cdot}809\, D}{L}\left[\frac{SL^2}{D}\right]^{1/3}. \qquad (17)$$

Substituting from Equations (13) and (14), the time-average mass transfer coefficient becomes

$$\bar{k}_{\mathrm{Vib}} = \frac{0{\cdot}809\, D^{2/3} A^{1/3} \omega^{3/2}}{\nu^{1/6} L^{1/3}} \\ \times \left|\frac{4}{\pi}\int_{\pi/4}^{5\pi/4}\left\{\cos\left(\omega t + \frac{\pi}{4}\right)\right\}^{1/3} \mathrm{d}t\right| \\ = \frac{0{\cdot}809\, D^{2/3} A^{1/3} \omega^{1/2}}{\nu^{1/6} L^{1/3}}. \qquad (18)$$

3. Comparison of proposed mechanisms with experimental data

There is considerable information concerning the effect of electrode vibration on the rate of mass transfer in electrolytes [1, 17, 33–41]. Unfortunately, in the majority of these investigations [33–39] bodies of revolution, such as cylinders and spheres, were used. With such shapes mass transfer enhancement is mainly due to the onset of steady secondary flows, (acoustic streaming), which result from the interaction of viscous and inertial effects in the boundary layer [42].

In most experimental investigations with flat plates, they were subjected to transverse vibrations normal to their plane [1, 40, 41]. The rate of mass transfer in these systems depends on the degree of turbulence produced as the liquid is displaced from the forward to the rear side of the plate, and would thus be most intense near the edge and dampened out as the centre of the plate is approached. This phenomenon explains why smaller transfer coefficients were obtained near the plates centre [41] and could also explain similar observations made recently [1]. On the other hand, data obtained using electrodes vibrated parallel to their surface [2, 43] and in which special precautions were made to eliminate edge turbulence, lend themselves well to comparison with the various proposed mechanisms.

These data (Figs. 1 and 2) indicate that the rate of mass transfer increases with increasing vibration intensity, i.e. with increasing frequency or amplitude. The peaks observed at certain frequencies most probably result from a resonance phenomenon as indicated by their occurence at accelerations of approximately 310 cm s^{-1} (Fig. 3). Similar resonance observations were made during the investigation of corrosion at vibrating surfaces [13, 14].

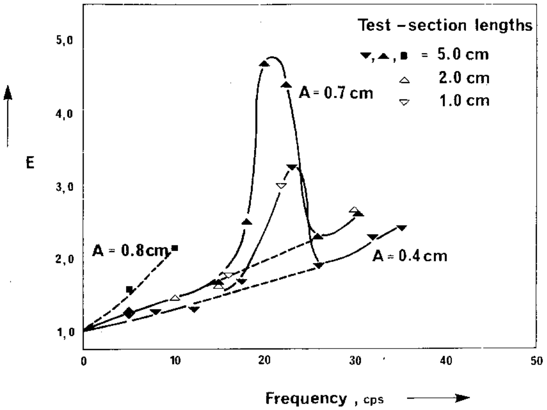

Fig. 1. Effect of large-amplitude oscillations on mass transfer enhancement.

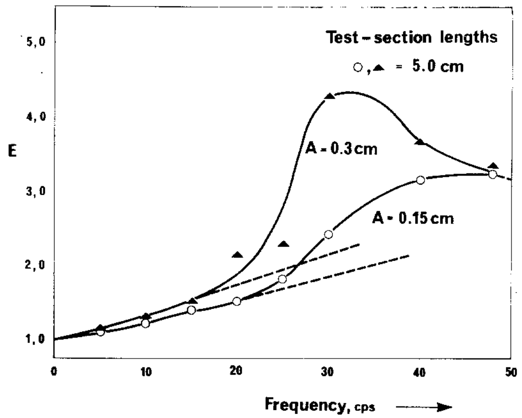

Fig. 2. Effect of small-amplitude oscillations on mass transfer enhancement.

Outside the peak region, mass transfer results are correlated by

$$\bar{k}_{\text{Vib}} = 1{\cdot}32 \times 10^{-5} A^{0{\cdot}42} F^{1{\cdot}09} \qquad (19)$$

This correlation differs from the predictions of the

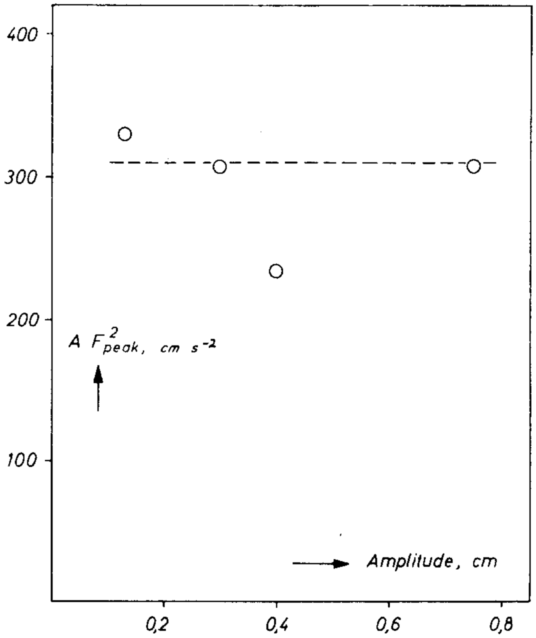

Fig. 3. Resonance conditions.

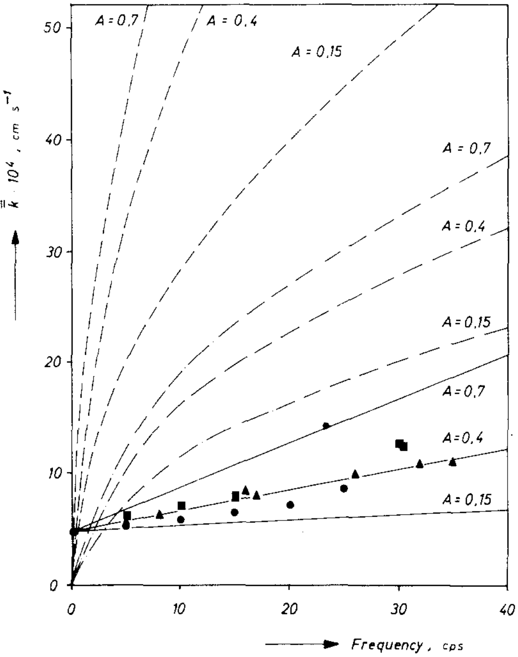

Fig. 4. Comparison between experimental results and proposed mechanisms. ● A = 0·15 cm; ▲ A = 0·4 cm; ■ A = 0·7 cm. – – – – Quasi steady model; —·— Oscillating concentration and velocity fields; ——— Stretched-film concept.

boundary-layer thinning mechanism (Equation 6) in both frequency and amplitude dependencies; thus indicating that this mechanism does not give a good representation of what is taking place at vibrating electrodes.

Fig. 4 presents a comparison between the remaining mechanisms and the experimentally determined values of the transfer coefficient outside the peak regions. The quasi steady-state mechanism shows the greatest deviation from experimental data. This is probably due to the lack, particularly at the small A/L ratios investigated, of the conditions necessary for this mechanism to be valid.

Much better agreement between theory and experiment is obtained when both the velocity and concentration oscillations are taken into consideration (Equation 18) but the predicted values are systematically higher than those experimentally obtained. This deviation most probably arises from the inapplicability of boundary conditions (Equation 12, II and III); better agreement with this analysis is expected at large A/L values where those boundary conditions are met. In this regard, it is interesting to notice that the peak values of $\bar{k}_{\mathrm{Vib}}$, occuring at resonance conditions, lie very close to predictions particularly at large amplitudes.

The experimental data were fitted to the expression derived on the basis of the stretched-film concept (Equation 5). As can be seen from Fig. 4, this concept yields good agreement with the data but tends to overemphasize the influence of vibrational amplitude on the rate of mass transfer. Thus predicted values for $A = 0{\cdot}7$ are higher than the experimentally observed ones, whereas for $A = 0{\cdot}15$, they are lower.

The success of the stretched-film concept in correlating the experimental data is surprising in view of the fact that it is an oversimplification of the physical situation; however, it was also found to correlate successfully the rate of corrosion at vibrating surfaces [14].

4. Conclusions

The application of oscillatory flows to electrochemical processes results in an increase of the rate of mass transfer and in a deposit of better quality. Several mechanisms have been presented to which this phenomenon could be attributed.

Attribution of the mass transfer enhancement to boundary-layer thinning results in an expression that fails to agree with experimentally observed trends. Mechanisms based on the concept of a quasi steady-state, or in which the oscillating velocity and concentration fields were taken into consideration, gave rise to smaller deviations but the agreement with experimental data was insufficient to accept either. On the other hand, the stretched-film concept was most successful in correlating the data in spite of the fact that it presents an oversimplified picture of the physical situation.

Mass transfer peaks occurring at certain frequencies most probably result from the occurrence of a resonance phenomenon.

Further work now underway should give a better understanding of this important, but complex, process.

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