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Electrolysis by intermittent potential

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The application of an intermittent potential yields the maximum rate of electrolysis under non-d.c., mass transfer controlled conditions. A numerical solution was obtained to calculate the average current density under the intermittent potential condition. It is shown that the maximum rate of electrolysis for the intermittent potential case and consequently for all non-d.c. cases cannot exceed that under d.c. conditions.

List of symbols

c	concentration of the reacting ion
c_∞	concentration of the reacting ion in the bulk
C	dimensionless concentration defined in Equation 6
D	diffusion coefficient
$(i_{\mathrm{d.c.}})_\mathrm{l}$	the d.c. limiting current density
$(\bar{i}_{\mathrm{int}})_\mathrm{l}$	average limiting current density under intermittent potential conditions
t	time
z	axial co-ordinate

Greek

$\alpha_{n_1}, \alpha_{n_3}$ β_{n_2}	coefficients of the series in Equations 1 12, 13 and 16
δ	Nernst diffusion layer thickness
ζ	dimensionless axial co-ordinate defined in Equation 6
$\lambda_{n_1}, \lambda_{n_3}$	constants defined in Equation 14
μ_{n_2}	constant defined in Equation 15
τ	dimensionless time defined in Equation 6
τ_1, τ_c	dimensionless on-period and cycle period, respectively

1. Introduction

There is a considerable amount of confusion in the literature concerning the maximum rate of electrolysis under non-d.c. conditions. For instance, Ozerov *et al.* [1] claimed that the rate of electrolysis could be increased indefinitely in pulsed electrolysis by decreasing the duration of the pulsed current. However, Cheh [2] and more recently, Viswanathan *et al.* [3] showed that although the magnitude of the instantaneous applied current could be considerably higher than that of d.c. electrolysis under mass transfer controlled conditions, the limiting overall electrolysis rate was in general lower. In electrodeposition practice, Avila and Brown [4] reported that a faster deposition rate could be achieved by pulsed electrolysis. The apparent inconsistency can be resolved to a large extent by considering the following viewpoints. The maximum rate of electrolysis of a single ion is reached at an applied current density which causes the concentration of the ion first to become zero at the electrode–solution interface. This current density is defined as the limiting current density by theoretical electrochemists. Cheh [2] has extended this concept to pulsed electrolysis by defining the limiting current density as the current density that causes the lowest surface concentration of the

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reacting ion to be zero. However, in electrodeposition practice, the limiting current density for deposition is defined as the maximum current density for which an acceptable deposit may still be obtained. Consequently, the true maximum rate of electrolysis is generally higher than the limiting rate as defined by electroplaters. Due to the improved deposit properties obtained by pulsed electrolysis, it is therefore possible for the optimum deposition rate under pulsed conditions to exceed that under d.c. conditions. Most recently, Ibl *et al.* [5] reported the application of very short pulses of current densities which were many orders of magnitude larger than practical d.c. current densities.

Among the three types of pulsed electrolysis, i.e., pulsed current, pulsed potential and intermittent potential, it can be stated that based on physical reasoning the application of intermittent potential leads to the maximum rate of electrolysis. This is because for the intermittent potential case the surface concentration of the reacting ion is always zero during the period when the potential is on (the on-period) whereas for the pulsed current case, the surface concentration of the reacting ion reaches zero only at the end of the on-period. Also, for reversible reactions, Viswanathan and Cheh [6] have shown that for the pulsed potential case, the polarity of the applied current is reversed as the potential of the electrode is changed. It is also interesting to note that the pulsed current and intermittent potential cases become identical to each other as both the on-period and the cycle time approach zero.

In this paper, a numerical solution was obtained to calculate the rate of electrolysis under intermittent potential conditions. The results were then compared with those from d.c. electrolysis.

2. Theoretical

Following the same approach as Cheh [2] with its justification as verified by Viswanathan *et al.* [3], the following diffusion equation is used to describe our system, under mass transfer controlled conditions

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} \tag{1}$$

where c is the concentration of the reacting species, D is its diffusion coefficient, t is time and z is the axial co-ordinate. For the case of intermittent potential, the boundary conditions are as follows:

$$c = c_\infty \quad \text{at } t = 0 \text{ and all } z \tag{2}$$

$$c = c_\infty \quad \text{at } t > 0 \text{ and } z = \delta \tag{3}$$

$$c = 0 \quad \text{at } z = 0 \text{ and } 0 < t \leqslant t_1,\ t_2 < t \leqslant t_3, \text{ etc.} \tag{4}$$

$$\frac{\partial c}{\partial z} = 0 \quad \text{at } z = 0 \text{ and } t_1 < t \leqslant t_2,\ t_3 < t \leqslant t_4, \text{ etc.} \tag{5}$$

where c_∞ is the bulk concentration of the reacting ion and δ is a distance from the electrode surface where the concentration of the reacting species is at its bulk value. For convective systems, δ may be interpreted as the thickness of the Nernst diffusion layer.

It is convenient to recast the problem in a dimensionless form by using the following dimensionless variables:

$$C = \frac{c}{c_\infty},\ \zeta = \frac{z}{\delta},\ \tau = \frac{Dt}{\delta^2}. \tag{6}$$

The dimensionless equation and boundary conditions are

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \zeta^2} \tag{7}$$

and

$$C = 1 \quad \text{at } \tau = 0 \text{ and all } \zeta \tag{8}$$

$$C = 1 \quad \text{at } \tau > 0 \text{ and } \zeta = 1 \tag{9}$$

$$C = 0 \quad \text{at } \zeta = 0 \text{ and } 0 < \tau \leqslant \tau_1,\ \tau_2 < \tau \leqslant \tau_3, \text{ etc.} \tag{10}$$

$$\frac{\partial C}{\partial \zeta} = 0 \quad \text{at } \zeta = 0 \text{ and } \tau_1 < \tau \leqslant \tau_2,\ \tau_3 < \tau \leqslant \tau_4, \text{ etc.} \tag{11}$$

It is also useful to define a dimensionless on period τ_1 by $\tau_1 = Dt_1/\delta^2$ and a dimensionless cycle time τ_c by $\tau_c = Dt_2/\delta^2$. The ratio of t_1/t_2 or τ_1/τ_c is known as the duty cycle in non-d.c. electrolysis.

Since it is well known in non-d.c. electrolysis that the transient part of the solution decays rather rapidly and the system reaches a periodic steady state after a few cycles [2], only the periodic steady state solution is sought in this paper.

By using the method of separation of variables [7], the following periodic steady state solution for Equation 7 subject to boundary conditions of Equations 8–11 can be obtained.

(a) During the on period, $0 < (\tau - \tau_{m-1}) \leqslant \tau_1$

$$C(\tau, \zeta) = \zeta + \sum_{n_1=1}^{\infty} \alpha_{n_1} \exp\left[-\lambda_{n_1}^2 (\tau - \tau_{m-1})\right] \sin(\lambda_{n_1} \zeta) \tag{12}$$

(b) During the off period, $\tau_1 < (\tau - \tau_{m-1}) \leqslant \tau_c$

$$C(\tau, \zeta) = 1 + \sum_{n_2=1}^{\infty} \beta_{n_2} \exp\left[-\mu_{n_2}^2 (\tau - \tau_{m-1})\right] \cos(\mu_{n_2} \zeta) \tag{13}$$

where α_{n_1} and β_{n_2} are the coefficients of the series and m is an odd index.

$$\lambda_{n_1} = n_1 \pi \tag{14}$$

$$\mu_{n_2} = (2n_2 - 1)\pi/2 \tag{15}$$

and

$$\begin{aligned} \alpha_{n_1} = {} & \frac{2}{\lambda_{n_1}} \\ & - 4 \sum_{n_2=2}^{\infty} \exp\left[-\mu_{n_2}^2 (\tau_c - \tau_1)\right] \frac{\lambda_{n_1}}{\mu_{n_2}^2 (\lambda_{n_1}^2 - \mu_{n_2}^2)} \\ & + 4 \sum_{n_2=1}^{\infty} \left[\sum_{n_3=1}^{\infty} \alpha_{n_3} \exp(-\lambda_{n_3}^2 \tau_1) \frac{\lambda_{n_3}}{(\lambda_{n_3}^2 - \mu_{n_2}^2)} \right] \\ & \times \frac{\exp\left[-\mu_{n_2}^2 (\tau_c - \tau_1)\right] \lambda_{n_1}}{(\lambda_{n_1}^2 - \mu_{n_2}^2)} . \end{aligned} \tag{16}$$

Equation 16 represents a recursion formula for α_{n_1}. For a chosen n_1, the right-hand side of Equation 16 is expanded for $n_3 = 1, 2, 3, \ldots L$ and summed over all possible values of n_2. By varying the values of n_1 from 1 to L we can generate L linear equations for the unknowns $\alpha_1, \alpha_2, \alpha_3, \ldots \alpha_L$.

In the present work, the series was truncated at a term whose magnitude is less than exp (− 15). Consequently, the value of L is given by

$$L = \text{nearest integer of} \left[\frac{1}{\pi} \left(\frac{15}{\tau_1} \right)^{\frac{1}{2}} \right] \tag{17}$$

For given values of τ_1 and τ_c, $\alpha_1, \alpha_2, \ldots \alpha_L$ can be calculated by using the Gauss–Jordan reduction method.

Once the α_{n_1}'s are known, Equation 12 can be used to calculate the concentration variation during the on-period of the cycle. The average limiting current density can then be calculated by using the method outlined by Cheh with the following result:

$$\frac{(\bar{i}_{\text{int}})_l}{(i_{\text{d.c.}})_l} = \frac{1}{\tau_c} \left\{ \tau_1 + \sum_{n_1=1}^{\infty} \alpha_{n_1} \frac{\left[1 - \exp(-\lambda_{n_1}^2 \tau_1)\right]}{\lambda_{n_1}} \right\} \tag{18}$$

where $(\bar{i}_{\text{int}})_l$ is the average limiting current density under intermittent potential conditions.

As τ_1 and τ_c approach zero, L increases rapidly and the number of equations for α_{n_1} to be solved becomes very large. For example, at the reasonable experimental conditions of applying 1 ms pulses with a 0·01 cm diffusion layer thickness and 10^{-5} cm^2 s^{-1} for the diffusion coefficient, τ_1 has the value of 10^{-4} and the number of equations which have to be solved is 123. Also, since α_{n_1} is dependent on the value of τ_1 and τ_c which vary with different experimental conditions, numerical tabulation of α_{n_1} at various values of τ_1 and τ_c is not suitable. It is therefore advantageous to seek approximate solutions with a reasonable degree of accuracy. To begin with, the upper and lower bounds for the rate of electrolysis under intermittent potential conditions are first derived in the following manner.

Assume that the d.c. limiting current electrolysis conditions prevail prior to the application of the intermittent potential. The concentration field is of course least uniform under the d.c. limiting current condition. The system is then open circuited and during the time period $(\tau_c - \tau_1)$, the current is zero. The concentration field for the following on-period can be obtained by solving Equation 1 subject to appropriate boundary conditions based on the known concentration profile. The average limiting current during the first cycle can then be calculated by

$$\begin{aligned} \left| \frac{(\bar{i}_{\text{int}})_l}{(i_{\text{d.c.}})_l} \right|_{\substack{\text{first}\\ \text{cycle}}} = {} & \\ & \frac{1}{\tau_c} \left\{ \tau_1 + \sum_{n_1=1}^{\infty} \frac{2}{\lambda_{n_1}^2} \left[1 - \exp(-\lambda_{n_1}^2 \tau_1)\right] \right. \\ & - \sum_{n_2=1}^{\infty} \sum_{n_1=1}^{\infty} \frac{2}{\mu_{n_2}^2} \exp\left[-\mu_{n_2}^2 (\tau_c - \tau_1)\right] \\ & \times \frac{2\left[1 - \exp(-\lambda_{n_1}^2 \tau_1)\right]}{(\lambda_{n_1}^2 - \mu_{n_2}^2)} . \end{aligned} \tag{19}$$

With additional cycles the number of terms on the right-hand side of Equation 19 grows. But by using the property of a convergent series one can derive an expression for the upper bound for the average limiting current density. The result is

$$\left.\frac{(\bar{i}_{\text{int}})_1}{(i_{\text{d.c.}})_1}\right|_{\text{upper}} = \frac{1}{\tau_c}\left\{\tau_1 + \frac{1}{3} - \sum_{n_2=1}^{\infty} \frac{2}{\mu_{n_2}^4}\exp\left[-\mu_{n_2}^2(\tau_c - \tau_1)\right]\right\}. \tag{20}$$

To derive the lower bound, let us recall the fact that the maximum rate of electrolysis under pulsed current conditions is always lower than that under intermittent potential conditions. Therefore, we can use the following limiting current expression for pulsed electrolysis [2, 3] as the lower bound

$$\left.\frac{(\bar{i}_{\text{int}})_1}{(i_{\text{d.c.}})_1}\right|_{\text{lower}} = (\tau_1/\tau_c) \times \left\{1 - 2\sum_{n=1}^{\infty} \frac{1}{\mu_n^2}\frac{[\exp(-\mu_n^2\tau_1) - \exp(-\mu_n^2\tau_c)]}{[1 - \exp(-\mu_n^2\tau_c)]}\right\}^{-1} \tag{21}$$

3. Results and discussion

The results are summarized in Figs. 1 and 2. Fig. 1 shows the average limiting current density under intermittent potential conditions as calculated by Equation 18 as a function of the dimensionless cycle time for different duty cycles. As τ_1 and τ_c become very large, the behaviour of the system approaches that of the d.c. limiting current condition. The maximum rate of electrolysis is then given by the product of the maximum d.c. electrolysis rate and the duty cycle.

For small values of τ_c, it is difficult to use Equation 18 to calculate the maximum rate of electrolysis. However, one can estimate the upper and lower bounds of the solution from Equations 20 and 21. The difference between these two bounds diminishes as the duty cycle is increased. Taking the average value for the two bounds as an approximation leads to satisfactory results. On the other hand, the difference between the estimates obtained by using the two bounds increases as the duty cycle is decreased. However, based on physical reasoning, one may conclude that as the duty cycle approaches zero, the results from the intermittent potential case are equivalent to that

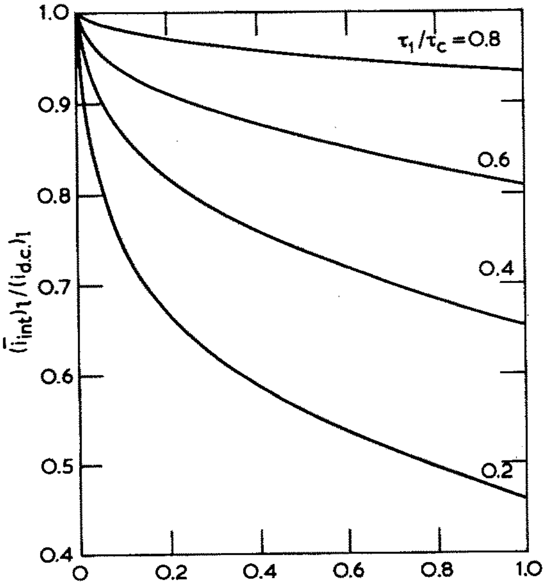

Fig. 1. The average limiting electrolysis rate under intermittent potential conditions.

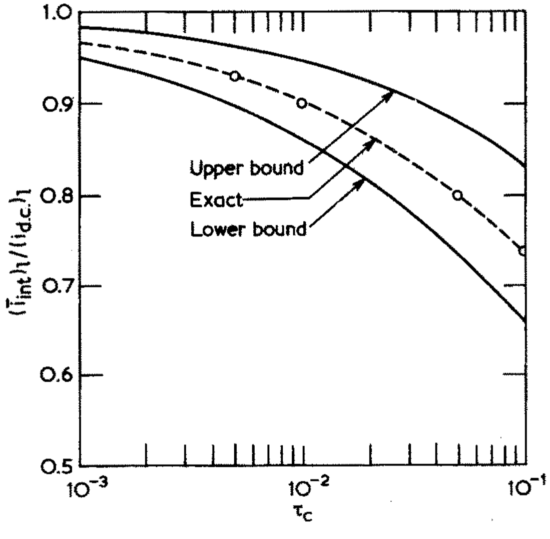

Fig. 2. The upper and lower bounds for average limiting electrolysis rate under intermittent potential conditions for short cycle times and a duty cycle of 0·2. The dashed line represents the exact solution.

from the pulsed current case. Fig. 2 is a numerical illustration of the theoretical results obtained by using Equations 20 and 21 at a duty cycle of 0·2 for small cycle times. The dashed line represents the results using Equation 18. It is seen that the average of the two bounds leads to a reasonable approximation of the numerical solution. For instance, even at the relatively large value of $\tau_c = 0{\cdot}1$, the estimated $(\bar{i}_{\text{int}})_l/(i_{\text{d.c.}})_l$ from an average of the upper and lower bounds is 0·745 whereas the exact value is 0·740. Of course, one should note that at $\tau_c \geqslant 0{\cdot}1$, Equation 18 can be used relatively easily to obtain an exact solution.

4. Conclusions

A numerical solution was obtained to calculate the average limiting current density under intermittent potential conditions. Due to the slow convergence of the numerical series for small values of on-period and cycle time, approximate methods based on estimating the upper and lower bounds of the numerical solution were also developed.

The most significant conclusion of this work is that the maximum rate of electrolysis under any non-d.c., mass transfer controlled conditions cannot exceed that from d.c. electrolysis.

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References

[1] A. M. Ozerov, N. P. Litvishko, I. N. Vavilina, P. M. Chervertnov, and Ya. E. Azak, *J. Appl. Chem. USSR* 39 (1966) 1632.

[2] H. Y. Cheh, *J. Electrochem. Soc.* **118** (1971) 551.

[3] K. Viswanathan, M. A. Farrell Epstein and H. Y. Cheh, *J. Electrochem. Soc.* **125** (1978) 1772.

[4] A. J. Avila and M. J. Brown, *Plating* 57 (1970) 1105.

[5] N. Ibl, J. Cl. Puippe and H. Angerer, *Surface Tech.* 6 (1978) 287.

[6] K. Viswanathan and H. Y. Cheh, *J. Appl. Electrochem.* 9 (1979) 537.

[7] H. F. Weinberger, 'A First Course in Partial Differential Equations', Blaisdell (1965).