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The application of pulsed potential and pulsed current to a rotating disc electrode system

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This paper is concerned with mass transfer to a rotating disc electrode (RDE) under pulsed potential and pulsed current conditions. For the case of pulsed potential, a numerical solution is presented to calculate the instantaneous current density for intermediate and large cycle times and an asymptotic solution for short cycle times. The special case of applying a step potential is then presented. The magnitude of the step current for a given transition time is calculated from the numerical solution by Viswanathan *et al.* for the pulsed current case. Comparison is made between the present results and various approximate solutions from the literature.

Nomenclature

c	concentration of reacting ion
c_i, c_∞	interfacial concentration and bulk concentration, respectively
C	dimensionless concentration defined in Equation 11
C_n, C_{n_1}, C_{n_2}	coefficients of an infinite series
D	diffusion coefficient of reacting ion
F	Faraday's constant
i	current density
i_{ave}	average current density over the entire cycle
$(i_{\text{dc}})_l$	d.c. limiting current density
i_{step}	step current density
K	dimensionless velocity defined in Equation 11
K_n	defined in Equation A5
n	number of electrons transferred
R_n	dimensionless concentration as a function of ζ
t	time
t_n	defined in Fig. 1
t_{tr}	transition time
v_z	axial velocity
z	axial co-ordinate
α	a dummy variable
β_n	defined in Equation 20
δ	thickness of the Nernst diffusion layer
ζ	dimensionless axial co-ordinate defined in Equation 12
$\lambda_{n_1}, \lambda_{n_2}$	eigenvalues
μ_n	defined in Equation 29
τ	dimensionless time defined in Equation 12
$\tau_1, \tau_c, \tau_{\text{tr}}$	dimensionless on-period, cycle period and transition time respectively
ψ	a function of axial co-ordinate defined in Equation A4

1. Introduction

The application of pulsed potential and pulsed current to practical systems has generated a considerable amount of interest in recent years. For instance, Despic and Popov [1] studied mass transfer under pulsed potential conditions in the absence of convection. Cheh [2] reported the application of pulsed current to gold electrodeposition. Sullivan [3] and Chen and Sautter [4] deposited cobalt under pulsed current conditions. Pavlovic *et al.* [5], Popov *et al.* [6] and Ibl *et al.* [7] studied the morphology of electrodeposits under pulsed conditions. Pulsed electrodeposition

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of copper was reported by Popov *et al.* [8] and more recently by Wan *et al.* [9].

Theoretical analyses of pulsed electrolysis were also reported in the recent literature. Popov *et al.* [8] studied mass transfer under pulsed conditions in both stirred and unstirred solutions. For the special case of applying a step potential to a RDE, there are a number of available approximate solutions. Filinovskii and Kiryanov [10] simplified their analysis by dropping the highest-order convective term. Buck and Keller [11] obtained a simple solution by neglecting convection altogether whereas Bruckenstein and Prager [12] assumed a linear concentration profile within a time-dependent mass transfer boundary layer in their study. For pulsed current electrolysis, an approximate solution on mass transfer has been reported by Cheh [2] who used a diffusion model originally studied by Rosebrugh and Miller [13] and by Pleskov and Filinovskii [14] who once again ignored the highest-order convective term in their work. Most recently, a numerical solution has been derived by Viswanathan *et al.* [15].

In this paper, a numerical solution for mass transfer to a RDE under pulsed potential conditions is presented. Results are compared with approximate solutions from the literature for the special case of applying a step potential. Also, the numerical solution for the pulsed current case by Viswanathan *et al.* [15] is used to compare with available solutions for the special case of a step current.

2. Theoretical

2.1. *Pulsed potential*

It is assumed that a RDE is situated in an electrolyte medium of large extent and the electrode is rotating at a constant velocity. The electrode reaction is assumed to be reversible. The radius of the RDE and the distance between the RDE and the counter electrode are both large compared to the thickness of the Nernst diffusion layer. The number of coulombs passed during an experiment is assumed to be so small that the depletion of the reacting species in the electrolyte can be neglected. An excess of supporting electrolyte is present so that electrical migration and non-faradaic effects are negligible. Finally, the Schmidt number of the system is much larger than unity so that the diffusion layer lies well within the momentum boundary layer. Under these conditions, the concentration of the reacting species is described by the following convective diffusion equation

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

with the following boundary conditions for the case of applying a pulsed potential

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

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

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

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

where c is the concentration of the reacting ion, c_∞ is its concentration in the bulk of the solution, D is the diffusion coefficient of the ion, v_z is the axial component of the fluid velocity, t is time, z is the axial co-ordinate extending from the electrode surface and t_n is defined in Fig. 1. Note that one may also consider that the applied

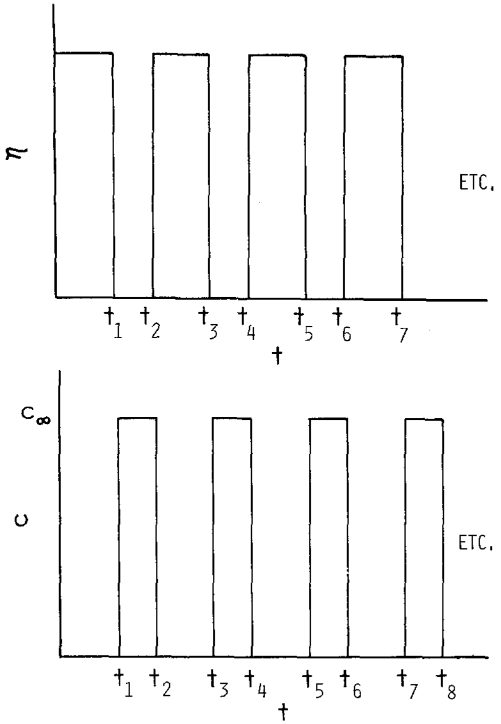

Fig. 1. Schematic diagrams of pulsed potential and surface concentration.

potential is at a certain value when $t_{m-1} < t \leqslant t_m$ but at a different value when $t_m < t \leqslant t_{m+1}$ where m is an odd number.

The method of solution for this problem except at very fast cycle times is similar to the one used by Viswanathan *et al.* [15]. Following the same approach, Equations 1–5 are first transformed into the following dimensionless form

$$\frac{\partial C}{\partial \tau} - K\zeta^2 \frac{\partial C}{\partial \zeta} = \frac{\partial^2 C}{\partial \zeta^2} \qquad (6)$$

and

$$C = 1 \quad \text{at } \tau = 0 \text{ and all } \zeta \qquad (7)$$

$$C = 1 \quad \text{at } \tau > 0 \text{ and } \zeta \to \infty \qquad (8)$$

$$C = 0 \quad \text{at } \zeta = 0 \text{ and } 0 < \tau \leqslant \tau_1, \tau_2 < \tau \leqslant \tau_3, \text{etc.} \qquad (9)$$

$$C = 1 \quad \text{at } \zeta = 0 \text{ and } \tau_1 < \tau \leqslant \tau_2, \tau_3 < \tau \leqslant \tau_4, \text{etc.} \qquad (10)$$

with the dimensionless variables defined by

$$C = \frac{c}{c_\infty}, \quad K = -\frac{v_z \delta^3}{\zeta^2 D} \qquad (11)$$

$$\tau = \frac{Dt}{\delta^2}, \quad \zeta = \frac{z}{\delta}, \quad \tau_n = \frac{Dt_n}{\delta^2} \qquad (12)$$

where δ is the thickness of the Nernst diffusion layer.

By substituting the Levich expressions [16] for v_z and δ for the infinite (Sc) condition, K turns out to be a constant, 2·136, independent of the physical properties of the electrolyte as well as the rotation speed.

For numerical solution in terms of a series, the boundary condition, Equation 8, may be modified as follows

$$C = 1 \quad \text{at } \tau > 0 \text{ and } \zeta = 2. \qquad (13)$$

The justification of this modification was suggested by Riddiford [17] and its effect on the solution of the problem has been discussed by Viswanathan *et al.* [15].

A series solution to Equation 6 is assumed as follows:

$$C(\tau, \zeta) = \sum_{n=0}^{\infty} C_n R_n(\zeta) \exp(-\lambda_{n_1}^2 \tau) \qquad (14)$$

where λ_{n_1} is the eigenvalue and C_n is the coefficient of the series. The solution corresponding to $\lambda_{n_1} = 0$ satisfies the inhomogeneous part of the boundary conditions, Equations 10 and 13. It is derived to be

$$R_0 = \int_0^{\zeta} \exp(-K\alpha^3/3)\,\mathrm{d}\alpha \qquad (15)$$

where α is a dummy variable. This equation represents physically the steady-state d.c. solution.

The solution corresponding to $\lambda_{n_1} \neq 0$ is obtained by using a fourth-order Runge–Kutta method. Details of the calculation are presented in the Appendix. The first twenty coefficients and eigenvalues are listed in Table 1.

From a knowledge of these coefficients and eigenvalues, the flux of the reacting species at the electrode surface under a periodic-state condition can be calculated from the following equations:

During the $\tau_{m-1} < \tau \leqslant \tau_m$ period

$$\frac{i}{(i_{\mathrm{dc}})_1} = 1 + \sum_{n=1}^{\infty} C_{n_1} \exp[-\lambda_{n_1}^2(\tau - \tau_{m-1})] \times \frac{\{1 - \exp[-\lambda_{n_1}^2(\tau_c - \tau_1)]\}}{[1 - \exp(-\lambda_{n_1}^2 \tau_c)]} \qquad (16)$$

During the $\tau_m < \tau \leqslant \tau_{m+1}$ period

Table 1. Eigenvalues and coefficients of Equation 16

n	C_{n_1}	λ_{n_1}
1	1·023 09	2·406 24
2	0·890 80	3·881 58
3	0·907 75	5·285 47
4	0·930 54	6·730 62
5	0·960 32	8·216 74
6	0·963 69	9·728 77
7	0·981 56	11·256 95
8	0·976 95	12·795 43
9	0·990 81	14·341 06
10	0·983 28	15·891 60
11	0·995 60	17·445 85
12	0·986 80	19·002 80
13	0·998 44	20·562 06
14	0·989 01	22·122 92
15	1·000 33	23·685 15
16	0·990 60	25·248 53
17	1·001 79	26·812 85
18	0·991 93	28·378 00
19	1·003 12	29·943 89
20	0·993 27	31·510 40

$$\frac{i}{(i_{\mathrm{dc}})_{\mathrm{l}}} = -\sum_{n=1}^{\infty} C_{n_1} \exp\left[-\lambda_{n_1}^2(\tau-\tau_m)\right] \times \frac{\left[1-\exp\left(-\lambda_{n_1}^2\tau_1\right)\right]}{\left[1-\exp\left(-\lambda_{n_1}^2\tau_{\mathrm{c}}\right)\right]} \tag{17}$$

where i is the instantaneous current density, $(i_{\mathrm{dc}})_{\mathrm{l}}$ is the d.c. limiting current density and τ_{c} is the dimensionless cycle time.

Although Equations 16 and 17 are in principle applicable to all cycle times, the slow convergence at values of $(\tau-\tau_m)$ or $(\tau-\tau_{m-1})$ less than 0·01 makes them impractical for fast cycles. A review of the physical phenomena shows that the effect of convection diminishes rapidly at fast pulses. Consequently, a simple diffusion model which is based on dropping the convective term $[-K\zeta^2(\partial C/\partial\zeta)]$ in Equation 6 and replacing the condition $\zeta \to \infty$ by $\zeta = \delta$ in Equation 8 should be applicable. The solution based on the simple diffusion model is available from Carslaw and Jaeger [18]:

During the $\tau_{m-1} < \tau \leqslant \tau_m$ period

$$\frac{i}{(i_{\mathrm{dc}})_{\mathrm{l}}} = 1 + 2\sum_{n=1}^{\infty} \exp\left[-\beta_n^2(\tau-\tau_{m-1})\right] \times \frac{\left\{1-\exp\left[-\beta_n^2(\tau_{\mathrm{c}}-\tau_1)\right]\right\}}{\left[1-\exp\left(-\beta_n^2\tau_{\mathrm{c}}\right)\right]} \tag{18}$$

During the $\tau_m < \tau \leqslant \tau_{m+1}$ period

$$\frac{i}{(i_{\mathrm{dc}})_{\mathrm{l}}} = -2\sum_{n=1}^{\infty} \exp\left[-\beta_n^2(\tau-\tau_m)\right] \times \frac{\left[1-\exp\left(-\beta_n^2\tau_1\right)\right]}{\left[1-\exp\left(-\beta_n^2\tau_{\mathrm{c}}\right)\right]} \tag{19}$$

where

$$\beta_n = n\pi. \tag{20}$$

A comparison between Equations 16 and 17, and Equations 18 and 19 showed that at $(\tau-\tau_{m-1})$ or $(\tau-\tau_m) = 0{\cdot}01$ the difference of $i/(i_{\mathrm{dc}})_{\mathrm{l}}$ calculated by the two sets of equations is less than 1% for all possible combinations of τ_1 and τ_{c}. Consequently, it is recommended that Equations 16 and 17 be used for $(\tau-\tau_{m-1})$ or $(\tau-\tau_m) \geqslant 0{\cdot}01$ whereas Equations 18 and 19 be used for $(\tau-\tau_{m-1})$ or $(\tau-\tau_m) < 0{\cdot}01$.

Two interesting conclusions are worth noting here. Firstly as shown by Equations 18 and 19, during the step change of potential, the sign of the current reverses. Secondly, the ratio of the overall electrolysis rate by pulsed potential to the d.c. electrolysis rate is equal to the duty cycle of the pulse. In other words, from Equations 18 and 19, one may show that

$$\frac{i_{\mathrm{ave}}}{(i_{\mathrm{dc}})_{\mathrm{l}}} = \frac{1}{\tau_{\mathrm{c}}}\left[\int_{\tau_{m-1}}^{\tau_m} \left(\frac{i}{(i_{\mathrm{dc}})_{\mathrm{l}}}\right)_{\mathrm{Eq.18}} \mathrm{d}\tau + \int_{\tau_m}^{\tau_{m+1}} \left(\frac{i}{(i_{\mathrm{dc}})_{\mathrm{l}}}\right)_{\mathrm{Eq.19}} \mathrm{d}\tau\right] = \frac{\tau_1}{\tau_{\mathrm{c}}} \tag{21}$$

2.2. *Step potential*

We now proceed to compare the present numerical solution to the approximate solutions from the literature for the case of applying a step potential. Equations used in this calculation are summarized as follows:

Present solution

$$\frac{i}{(i_{\mathrm{dc}})_{\mathrm{l}}} = 1 + \sum_{n=1}^{\infty} C_{n_1} \exp\left(-\lambda_{n_1}^2\tau\right) \tag{22}$$

Filinovskii and Kiryanov's solution [10]

$$\frac{i}{(i_{\mathrm{dc}})_{\mathrm{l}}} = \frac{\exp(-3{\cdot}1\tau)}{(\pi\tau)^{1/2}} + 0{\cdot}94\,\mathrm{erf}\,(3.1\tau)^{1/2} \tag{23}$$

Buck and Keller's solution [11]

$$\frac{i}{(i_{\mathrm{dc}})_{\mathrm{l}}} = 1 + 2\sum_{n=1}^{\infty} \exp\left(-n^2\pi^2\tau\right) \tag{24}$$

Bruckenstein and Prager's solution [12]

$$\tau = \frac{1}{6}\left(\frac{1{\cdot}8049}{1{\cdot}6116}\right)^2\left\{\frac{1}{2}\ln\left[\frac{(1-R^3)}{(1-R)^3}\right] + \sqrt{3}\left[\frac{\pi}{6} - \tan^{-1}\left(\frac{2R+1}{\sqrt{3}}\right)\right]\right\} \tag{25}$$

where

$$R = (i_{\mathrm{dc}})_{\mathrm{l}}/i \tag{26}$$

A numerical comparison for the four solutions is shown in Table 2. Filinovskii and Kiryanov's result shows good agreement with the numerical solution up to $\tau = 0{\cdot}5$. It begins to deteriorate at large τ values due to the increasing importance of convection. Buck and Keller's solution consistently underestimates the ratio of $i/(i_{\mathrm{dc}})_{\mathrm{l}}$ although the accuracy of the solution improves at small values of τ. This is because of the diminishing role of convection at short cycle times. Bruckenstein and Prager's solution shows very good agreement with the numerical solution. The discrepancy is less than

Table 2. Comparison between three approximate solutions and the present results for current transients at different values of time

τ	$i/(i_{dc})_l$			
	Present results	*Filinovskii and Kiryanov* [10]	*Buck and Keller* [11]	*Bruckenstein and Prager* [12]
0·02	4·000	4·008	3·989	3·972
0·04	2·842	2·851	2·821	2·825
0·06	2·335	2·343	2·303	2·324
0·08	2·038	2·044	1·995	2·030
0·10	1·838	1·843	1·784	1·834
0·20	1·369	1·369	1·279	1·375
0·40	1·103	1·090	1·039	1·115
0·60	1·032	1·003	1·005	1·041
0·80	1·010	0·968	1·001	1·016
1·00	1·003	0·953	1·000	1·006

1·2% for the range of τ values used in the calculation. Experimental verification for the step potential case was reported by Bruckenstein and Prager [12].

2.3. *Step current*

A numerical solution for applying a pulsed current to a RDE system has recently been presented by Viswanathan *et al.* [15]. We now present a comparison of the numerical solutions to two approximate solutions from the literature for the special case of applying a step current to the RDE. When a step current is applied, both the concentration of the reacting species at the surface and the electrode potential changes with time. An important quantity to characterize mass transfer is the transition time t_{tr} which is defined as the time elapsed to when the concentration of the reacting species becomes zero at the electrode–solution interface. The numerical comparison is made for the magnitude of the step current based on different solutions for a given transition time. Equations used in this calculation are summarized as follows:

Viswanathan *et al.*'s solution [15]

$$\frac{i_{step}}{(i_{dc})_l} = \left[1 - \sum_{n=1}^{\infty} C_{n_2} \exp(-\lambda_{n_2}^2 \tau_{tr})\right]^{-1} \tag{27}$$

where C_{n_2} and λ_{n_2} are the coefficients and eigenvalues of the series in Equation 26. Their values have been tabulated by Viswanathan *et al.* [15].

Cheh's solution [2]

$$\frac{i_{step}}{(i_{dc})_l} = \left[1 - 2\sum_{n=1}^{\infty} \frac{\exp(-\mu_n^2 \tau_{tr})}{\mu_n^2}\right]^{-1} \tag{28}$$

where

$$\mu_n = (2n-1)\pi/2 \tag{29}$$

Pleskov and Filinovskii's solution [14]

$$\frac{i_{step}}{(i_{dc})_l} = [1{\cdot}07\, \mathrm{erf}\,(3{\cdot}1\tau_{tr})^{1/2} - 0{\cdot}73 \exp(-1{\cdot}65\tau_{tr})\, \mathrm{erf}\,(1{\cdot}45\tau_{tr})^{1/2}]^{-1} \tag{30}$$

A numerical comparison between the three models is shown in Table 3. Both approximate solutions agree well with the numerical solution at short transition times. The maximum discrepancy between Cheh's solution and the numerical solution is less than 4% for all values of τ_{tr} whereas that between Pleskov and Filinovskii's solution and the numerical solution is less than 1% for $\tau_{tr} < 0{\cdot}5$. It is worth noting here that at very short transition times, Equation 28 reduces to

$$i_{step} = \frac{nFc_\infty}{2} \frac{(\pi D)^{1/2}}{t_{tr}^{1/2}} \tag{31}$$

which is the well-known Sand equation. Kriglikov *et al.* [19, 20] measured transition times under galvanostatic conditions at a rotating Pt electrode in alkaline $K_3Fe(CN)_6$ solution and found a linear relation between i versus $t_{tr}^{-1/2}$ for small values of time in accordance with Equation 31. For large

Table 3. Comparison between two approximate solutions and the present results for the magnitude of step current at different values of transition time

τ_{tr}	$i_{step}/(i_{dc})_l$		
	Present results	*Cheh* [2]	*Pleskov and Filinovskii* [14]
0·001	27·990	28·025	27·891
0·005	12·532	12·533	12·477
0·010	8·864	8·862	8·826
0·050	3·974	3·963	3·961
0·100	2·824	2·803	2·816
0·200	2·024	1·984	2·019
0·400	1·488	1·433	1·480
0·600	1·276	1·226	1·263
0·800	1·167	1·127	1·147
1·000	1·105	1·074	1·077
1·200	1·067	1·044	1·032
1·400	1·043	1·026	1·003
1·600	1·028	1·016	0·983
1·800	1·019	1·010	0·969
2·000	1·012	1·006	0·959

values of t_{tr}, the transition time was found to depend on the rotation speed.

3. Conclusions

A numerical solution was obtained for mass transfer to a RDE system under pulsed potential conditions. A quantitative comparison was made between the present solution and a number of approximate solutions for the special case of applying a step potential. Also, a numerical solution for calculating the magnitude of the step current as a function of transition time was presented. Results were compared quantitatively with two approximate solutions.

Appendix

Solution for $\lambda_{n_1} > 0$

Substitution of Equation 14 into Equation 6 yields

$$\frac{d^2R_n}{d\zeta^2} + K\zeta^2\,\frac{dR_n}{d\zeta} + \lambda_{n_1}^2 R_n = 0. \qquad \text{(A1)}$$

The boundary conditions are

$$R_n = 0 \qquad \text{at } \zeta = 0 \qquad \text{(A2)}$$

$$R_n = 0 \qquad \text{at } \zeta = 2 \qquad \text{(A3)}$$

Let

$$\psi_n(\zeta) = \frac{R_n}{K_n}\,e^{K\zeta^3/6} \qquad \text{(A4)}$$

where

$$K_n = \left.\frac{dR_n}{d\zeta}\right|_{\zeta=0}. \qquad \text{(A5)}$$

Introduction of Equation A4 into Equation A1 gives

$$\frac{d^2\psi_n}{d\zeta^2} + \left(\lambda_{n_1}^2 - K\zeta - \frac{K^2\zeta^4}{4}\right)\psi_n = 0 \qquad \text{(A6)}$$

and the boundary conditions are

$$\psi_n = 0 \qquad \text{at } \zeta = 0 \qquad \text{(A7)}$$

$$\psi_n = 0 \qquad \text{at } \zeta = 2 \qquad \text{(A8)}$$

$$\frac{d\psi_n}{d\zeta} = 1 \qquad \text{at } \zeta = 0 \qquad \text{(A9)}$$

The eigenvalue λ_{n_1} is obtained by solving Equation A6 subject to all the boundary conditions by a trial-and-error fourth order Runge–Kutta method. The concentration profile is then given by

$$C(\tau, \zeta) = \int_0^{\zeta} e^{-K\alpha^3/3}\, d\alpha + \sum_{n=1}^{\infty} C_{n_1} \psi_n(\zeta)\, e^{-K\zeta^3/6}\, e^{-\lambda_{n_1}^2 \tau} \tag{A10}$$

where

$$C_{n_1} = C_n K_n. \tag{A11}$$

The coefficient C_{n_1} is determined by using the following relation.

$$C_{n_1} = \frac{\int_0^2 \left(1 - \int_0^{\zeta} e^{-K\alpha^3/3}\, d\alpha\right) \psi_n(\zeta)\, e^{K\zeta^3/6}\, d\zeta}{\int_0^2 \psi_n^2(\zeta)\, d\zeta} \tag{A12}$$

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