OPTIMAL PULSE SHAPES FOR PERIODIC REVERSE ELECTROPLATING *

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Abstract – In this report, time-dependent carrier concentration in electrolytic cells, due to some basic periodic shapes of excitation signal, has been studied. Exact analytical solutions for step, sinusoidal and periodic pulse reverse inputs are derived. The effect of frequency, forward and reverse amplitudes, and duty cycle are investigated. An analytical solution of the model is obtained as Fourier series using Laplace transformations applied to a one-dimensional model with linearized Butler-Volmer electrode kinetics. The results are applied to an acid-copper bath. It is shown that optimal operation points exist. Optimal current waveforms for obtaining efficient and enhanced deposition process, and faster deposition rate compared to simple DC electroplating is discussed.

Keywords – Electroplating, Laplace transformation, diffusion, optimization, electrolyte, Butler-Volmer

1. INTRODUCTION

A good electro-deposit layer is characterized with some qualitative features such as uniformity, adhesion, low porosity, low residual stress, brightness and throwing power [1]. One of the most important problems in obtaining such deposits is that the electrolytic processes are usually in the transport limited regimes. More exactly, the electrode diffusion layer limits the rate of carrier transport, and thus several features of the deposit are affected. Generally speaking, for getting a better deposit, usually the thickness of the electrode diffusion layer has to be reduced.

There are several steady and non-steady methods to achieve this goal. One of the major non-steady methods is to apply an alternating current (AC) voltage to electrodes instead of a direct current (DC) voltage. The input voltage can have any pulse shape with a non-zero average, and a frequency between several tens of Hertz and hundreds of Kilo-hertz. Pulse-plating have found applications in plating of alloys [1-3], thin films [4], and even decorative coatings [5]. In the pulse-plating, general improvements in the quality and hardness of the plates and net plating speed have been reported [1, 2]. Several studies have addressed the time-dependent carrier concentration and transport in pulse plating methods for some basic waveforms [6-10], using the simple diffusion model reported in [11]. For this method mass transfer requirements are addressed in [12]. It has been observed that the bath’s efficiency may also decrease under pulse periodic plating [13]. The effect of off-time in the pulse shape during pulse plating of Cu-Ni alloys has been studied in [14].

Bard and Faulkner, [10], have made an analytic study of controlled potential experiments and solved the diffusion equation for large and small-amplitude steps, reversible and irreversible

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processes in step-input experiments. They found expressions for the reversible Faradayic impedance of the cell corresponding to a sinusoidal excitation without a DC-bias, being proportional to the inverse root square of the frequency. Under such situations, all variations are supposed to be sinusoidal at small amplitudes. They also reported an equivalent circuit of the electrolytic cell. However, their model was based on the assumption that the system is controlled by a voltage source.

In this article, an analytical solution is derived describing a simple electroplating cell excited by a large-amplitude AC current source (the application of a current source instead of a voltage source can be practically realized by using proper electronic circuits). In this analysis, we assume that most of the current is carried by a single type of ion, and the frequency is much lower than the relaxation frequency of the electrolyte. The analyses of DC-biased sinusoidal and arbitrary shaped pulse-periodic waveforms are considered. The results of the latter case reveal that there exist optimal operating regions in which the enhancement and efficiency of the deposition process are both improved. Here, Enhancement is defined as the increase in the limiting current density under the applied conditions relative to the normal method (DC input) and efficiency is the ratio of the useful electric current carried by deposited ions to the total transferred charge in positive and negative cycles of current. In other words, the ratio of the forward to the reverse amplitudes and the duty cycles may be chosen for some optimal values at which the enhancement and efficiency of the bath simultaneously increase. In this situation, the plating speed may be optimized to take a considerably higher rate than the usual DC plating. In addition, simple expressions for linearized electric impedance are also derived for each case.

2. SYSTEM DESCRIPTION

An overview of system is illustrated in Fig. 1. The distance between two electrodes is assumed to be 2L. A current density of \( i = i(t) \) is supposed to be carried by a single type of carrier in which its local time-dependent concentration between the electrodes is \( C(z,t) \). The model is described by the diffusion of carriers, or the so-called Fick's second law [11, 15]

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2}
\]  

(1)

![Fig. 1. The profile of current density between electrodes in the simple electrolytic cell](image)

The electric current density generally results from two different mechanisms similar to the carrier transport in semiconductors [16]. The first mechanism is based on the local density imbalance of carriers producing a net diffusion current. This current can be estimated by Fick's first law. The next mechanism is the drift of carriers resulting from the local electric field. Therefore, the total current can be found by summing up these two terms as
where $D$ is the diffusion constant, $n$ is the valence of ions, $F$ is the Faraday constant, $E$ is the electric field, $\mu$ is the mobility of ions and $e$ is the unit electronic charge. The accuracy of this diffusion model for prediction of the concentration of reacting species at the electrode surface under pulsed current analysis has been established in [17].

We assume that the drift term is about zero near the electrodes, since the electrode double layer reduces the mobility of carriers considerably. The main reason is that the electrode double layer consists of charged ions of opposite polarity and they scatter the charged carriers through coulomb collisions. Hence the diffusion process dominates the transport near the electrodes (for discussion on a method for determination of the thickness of this layer refer to [18]). Then from relation (2) the following boundary conditions are obtained

$$\frac{D}{z} \frac{\partial C}{\partial z} \bigg|_{z=L} = \frac{D}{z} \frac{\partial C}{\partial z} \bigg|_{z=-L} = -\frac{i}{nF}$$

(3)

The model becomes complete with the addition of Butler-Volmer kinetics

$$i \cdot n = I_0 \left[ \exp\left(\frac{-\alpha_a nF \eta}{RT}\right) - \exp\left(\frac{\alpha_c nF \eta}{RT}\right) \right]$$

(4)

Here, $n$ is the normal vector to electrodes, $\alpha_a$ and $\alpha_c$ are the transfer ratios of anode and cathode, $\eta$ is the over potential, $R$ is the universal gas constant, $T$ is the absolute temperature, and $I_0$ is the exchange current density. Numerical values for the parameters introduced in (3) and (4) may be found in [19] for the acid-copper bath.

3. STEP INPUT ANALYSIS

We assume that the concentration of ions in the steady state and at the system’s geometrical center $z=0$ is $C_0$. In the perturbation analysis it is supposed that

$$C(z,t) = C_0 + \delta C(z,t) = C_0 [1 + \delta(z,t)]$$

(5)

By putting (5) in the diffusion Eq. (1) and applying boundary conditions (3) it is found that

$$\delta(z,t) = \frac{-1}{C_0 nFD} L^{-1} \left\{ I(s) \left[ \frac{s}{D} \sinh \left( \frac{s}{D} z \right) \right] \right\}$$

(6)

In this stage, since the input is a step function, its Laplace transformation is given by

$$I(s) = \frac{I_0}{s}$$

(7)

The electric current approaches its limiting current density $i_L$ when $\delta(L,t) = -1$. $\delta(L,t)$ is found from relation (6) as

$$\delta(L,t) = \frac{-I_0 L}{C_0 nFD} - \frac{8I_0 L}{\pi^2 C_0 nFD} \sum_{k=1}^{\infty} \exp\left[ -\frac{D}{4L^2} \frac{(2k-1)^2 t}{(2k-1)^2} \right]$$

(8)
The steady state solution is obtained by taking the limit of the time variable \( t \) when it approaches infinity as

$$
\delta (L, \infty ) = - \frac{I_0}{C_0 nFD} \quad (9)
$$

The limiting current occurs at \( \delta = -1 \), where the concentration of carriers becomes zero. Smaller values for \( \delta \) correspond to a negative concentration of carriers, which is physically impossible. Thus the expression for the limiting current density is

$$
i_L = \frac{C_0 nFD}{L} \quad (10)
$$

Now a simple approximate expression for the linearized cell’s impedance may be found as follows.

The assumption of linear variations leads to small overpotential \( \eta \). Also the cell’s electromotive force (emf) may be obtained from

$$
emf = - \int Edz - \eta_a + \eta_c 
$$

in which \( \eta_a \) and \( \eta_c \) are the anodic and cathodic overpotentials which may be obtained from the linearized Butler-Volmer electrode kinetics (4) as

$$
\eta_c = \eta_a = \frac{RT}{nF(\alpha_a + \alpha_c)} i
$$

The electric field \( E \) may be obtained from (2) and (3) as

$$
E = \frac{nFD}{\mu en} \left( \frac{1}{1 + \delta} \left[ \frac{\partial \delta}{\partial z} \right]_{z=L} - \frac{\partial \delta}{\partial z} \right) 
$$

By assuming \( \delta << 1 \) and using Equation (11-13), \( emf \) is obtained

$$
emf = \frac{2RT}{nF(\alpha_a + \alpha_c)} i \quad (14)
$$

and the impedance of the linearized system results to be

$$
Z = \frac{2RT}{nF(\alpha_a + \alpha_c)} \quad (15)
$$

This relation shows that the DC impedance of the linearized system is independent of the mobility of the carriers. In other words, the electrical characteristic of the steady state DC system is determined by the diffusion and not by the drift mechanisms. In this case, the distribution of carriers becomes a linear function of position. The linearized DC impedance as given in the above relation is indeed of a non-ohmic origin, and determined solely by its electrochemical properties of the reactions at the electrode surfaces.

4. SINUSOIDAL INPUT ANALYSIS

When \( i(t) = I_0 + I_m \sin \omega t \), the above analysis is still valid except that
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\[ I(s) = \frac{I_0}{s} + \frac{I_m s}{s^2 + \omega^2} \]  

(16)

By putting (16) in (6), \( \delta(L, t) \) is calculated. We need only steady state response terms

\[ \delta(L, t) = -\frac{I_0}{i_L} - \frac{I_m}{L i_L} \sqrt{\frac{D}{\omega}} A(\omega) \times \sin \left( \omega t - \frac{\pi}{4} - \phi(\omega) \right) \]  

(17)

in which, \( i_L = C_0 nFD / L \) and

\[ A(\omega) = \sqrt{\frac{\cos^2 \frac{\omega L}{2D} - \cos^2 \frac{\omega L}{2D}}{\cosh^2 \frac{\omega L}{2D} - \sin^2 \frac{\omega L}{2D}}} \]  

(18)

and

\[ \phi(\omega) = \tan^{-1} \left[ \frac{\tan \frac{\omega L}{2D}}{\tanh \frac{\omega L}{2D}} \right] + \tan^{-1} \left[ \tan \frac{\omega L}{2D} + \tanh \frac{\omega L}{2D} \right] \]  

(19)

It is seen that in the limit of low and high frequencies \( (\omega \rightarrow 0 \) and \( \infty) \), \( A(\omega) \) and \( \phi(\omega) \) tend to constant values independent of \( \omega \). In small frequencies there is no enhancement with respect to DC state (Enhancement = 1). But in the large frequency limit, the steady state part of \( \delta(L, t) \) is given by

\[ \delta(L, t) = -\frac{I_0}{i_L} - \frac{I_m}{L i_L} \sqrt{\frac{D}{\omega}} \times \sin \left( \omega t - \frac{\pi}{4} - \frac{2\omega}{D} L \right) \]  

(20)

Putting \( \delta = -1 \), the limiting current density is related to \( I_m \) and the frequency of excitation as

\[ i_L = I_0 + I_m \left( \frac{1}{L} \sqrt{\frac{D}{\omega}} \right) \]  

(21)

This situation may be clarified if we rewrite the above as \( I_0 = 0 \)

\[ (I_m)_{\max} = L \sqrt{\frac{\omega}{D}} x i_L = \sqrt{\frac{\omega}{\omega_0}} x i_L \]  

(22)

\( \omega_0 = \frac{\omega}{L} \) is the frequency associated with the transit time across the bath. Equation (22) shows that in this case, the enhancement in the maximum current density is proportional to \( \sqrt{\omega} \).

Now the linearized impedance is derived. From (14), (15), and (20), the emf can be calculated as

\[ \text{emf} = 2 \left[ \frac{L}{\mu e n C_0} + \frac{RT}{nF \left( \alpha_0 + \alpha_v \right)} \right] I - \frac{2FD}{\mu e} \sqrt{\frac{D}{\omega}} \frac{A(\omega)}{L i_L} \exp \left[ -j \left( \frac{\pi}{4} + \phi \right) \right] I \]  

(23)

where the bar represents the complex phasor of the variable. Therefore the complex impedance of the system would be
$Z = 2 \left( \frac{L}{\mu n C_0} + \frac{RT}{n F (\alpha_a + \alpha_c)} + \frac{FD}{\mu e} \sqrt{\frac{D}{\omega L_i L}} \exp \left( j \left( \frac{3\pi}{4} - \phi(\omega) \right) \right) \right)$ \tag{24}

It is easy to observe the low frequency limit of the linearized impedance by taking the $\omega \to 0$ limit of the functions $A(\omega)$ and $\phi(\omega)$, which are respectively equal to $\sqrt{\frac{\omega L}{D}}$ and $\frac{\omega}{4}$. It is deduced that in low frequencies, $Z$ approaches the DC impedance $Z_{DC}$ as given in (15), which justifies the previous derivations.

In the limit of high frequencies ($\omega \gg \omega_0$), however

$Z = 2 \left( \frac{L}{\mu n C_0} + \frac{RT}{n F (\alpha_a + \alpha_c)} \right)$ \tag{25}

which shows that ohmic characteristics of the electrolytic cells play a role in non-steady platings, contrary to the previous result for steady-state DC plating.

5. PULSE INPUT ANALYSIS

In this section, it is assumed that the current has an arbitrary pulse shape shown in Fig.2. The period of signal is denoted by $T$ and the forward and reverse amplitudes are given by $A_f$ and $A_r$.

![Electric current waveform and the parameters](image)

The Laplace transform of the input signal may be easily shown to be

$F(s) = \frac{1}{s(e^{-st} - 1)} \times \left[ A_f + A_r e^{-st_f} - A_f - A_r e^{-st_r} \right]$ \tag{26}

Similar to the sinusoidal state analysis, $F(s)$ is inserted in (6) resulting in

$\delta(z,t) = -\frac{1}{C_0 n F D} \frac{1}{L} \left[ \sinh \frac{s z}{D} \left( A_f + A_r e^{-st_f} - A_f - A_r e^{-st_r} \right) \right] \left( \cosh \frac{s L}{D} \right)$ \tag{27}

For calculating the inverse Laplace transform in the above relation, its poles must be found. In the first multiplicand, a pole at $s=0$, corresponding to $\sqrt{s}$ term in the denominator cancels out with a zero at $s=0$ corresponding to the $\sinh$ term in the numerator. Similarly another pole at $s=0$ in the next multiplicand cancels out with a zero in its numerator. The $\cosh$ term produces zeros in the
denominator at \( s = -(k + \frac{1}{2} \pi)^+, k \in \mathbb{Z} \), with negative real part. However, these poles cannot contribute to the steady state solution since their associated time-domain terms would decay to zero.

Therefore, the poles influencing the steady state response of (27) are solely determined by the zeros of \( e^{-sT} - 1 \) which are given by

\[
s_k = -jk \frac{2\pi}{T}, \quad k \in \mathbb{Z}
\]

Finally, (27) may be rewritten in the following form

\[
\delta(z,t) = \frac{-1}{C_0 nFD} \sum_{k=-\infty}^{\infty} \text{Res} \left\{ \frac{\sinh \left( \frac{s_k}{D} z \right)}{\cosh \left( \frac{s_k}{D} L \right)} \times \frac{\left( A_f + A_p \right) e^{-sF} t_f - A_p e^{-sF} t_f}{s - e^{-sT} - 1} \right\} e^{sT}
\]

The steady state part of \( \delta(L,t) \) is given by

\[
\delta_{ss}(L,t) = \frac{-1}{C_0 nFD} \sum_{k=-\infty}^{\infty} \lim_{s \to s_k} \left\{ \frac{\tanh \left( \frac{s}{D} L \right)}{\frac{s}{D}} \left( s + \frac{2\pi}{T} \right) \times \left[ \left( A_f + A_p \right) e^{-sF} t_f - A_p e^{-sF} t_f \right] \right\} e^{sT}
\]

After some mathematical manipulations the above relation is transformed to a more convenient form

\[
\delta_{ss}(L,t) = \frac{-1}{C_0 nFD} \left\{ \frac{L}{A + 1} \left( \frac{Ax - 1 + x}{A + 1} \right) - 2 \sum_{k=1}^{\infty} \frac{3 \sin(k\pi x)}{k^2 \alpha \pi} \frac{\coth^2 \beta + \cot^2 \beta \cos \left( \frac{2\pi}{T} t + \frac{\pi}{4} + k\pi x + \tan^{-1} \left( \frac{2\beta}{\sin 2\beta} \right) \right)}{1 + \cot^2 \beta \cos^2 \beta} \right\}
\]

in which \( \alpha = \sqrt{2\pi/TD} \), \( \beta = L \alpha \sqrt{k/2} \), \( x = t_f/T \) and \( A = A_f/A_p \). Here, the imaginary part of (30) identically vanishes, since \( \delta_{ss}(L,t) \) should be pure real in order to have a physical meaning.

6. SIMULATION RESULTS AND DISCUSSIONS

The efficiency of the system as defined in the first section is mathematically given by

\[
\eta = \frac{\int i(t) dt}{\int t_i(t) dt} = \frac{A_f t_f A_p t_f}{A_f t_f A_p t_f} = \frac{x(A + 1) - 1}{x(A - 1) + 1}
\]

This parameter is a measure for the useful percentage of total moving current in both directions. For example, when the area in positive and negative cycles are equal, that is, no net mass transfer between the electrodes takes place, the value of efficiency becomes zero. Similarly, its positive and negative values correspond to a net electroplating and electropolishing processes, respectively. Obviously, its maximum and minimum values are +1 and -1; moreover, its value is independent of the excitation frequency.

The enhancement is defined as the ratio of the maximum absolute instantaneous current density to the DC limiting current density as given by (10). Mathematically, it can be written as

\[
\zeta = \frac{\max \{ |i(t)| \}}{I_L}
\]
It should be added that the enhancement parameter can take values equal to or larger than unity. In the limit of low frequencies, its value approaches its minimum, and in the limit of high frequencies, it increases indefinitely.

Actually, the efficiency reaches its maximum for DC currents. However, its quality may be improved by attaining higher enhancement at the same time. This is due to the fact that the electrolysis processes are usually in the transport limited regions. At higher frequencies in which the maximum possible passing current enhances, the system enters to the reaction rate limited regions. This region enjoys, however, of more uniform and higher quality deposits. Since most of the problems in the quality of plate have origins in mass transfer limitations. It is also discussed in the literature that pulse plating results in a higher quality and hardness of plates while permitting higher deposition rate [1,2].

Based on the discussions above, one of the optimization goals can be proposed as to choose a waveform with an efficiency as high as possible. The second optimization goal can be proposed as to choose a waveform with an enhancement as high as possible. These goals are here shown to be possible to be reached at once, by proper selection of electric current waveform. Then we proceed to define a parameter expressing the net enhancement in maximum permissible plating rate. It is shown that by optimized choice of the input waveform, this rate can be increased considerably compared to ordinary DC electroplating.

The numerical approach is straightforward. For a set of values for the ratio of forward to backward amplitudes \( A \) and the duty cycle \( x \), the efficiency is computed. The steady state system’s responses to the corresponding waveforms are computed in the time domain by the aid of above relations. Its maximum in one period is found numerically by comparing test points over a single period. Finally the result is divided to the limiting current density.

The result of the numerical calculation of the efficiency is shown in Fig. (3). The efficiency is plotted in terms of the duty cycle (varied between 0 and 1) and the ratio of forward to backward amplitudes (varied up to 10). It is observed that the efficiency takes non-positive values for some choices of the duty cycle and the ratio of forward to reverse amplitudes. In order to have a net electrodeposition, it is necessary to have positive values of efficiency.

![Efficiency vs Duty Cycle and Forward to Backward Amplitudes](image)

Fig. 3. Three dimensional plot of efficiency \( \eta \). Duty cycle varies between 0 and 1. Ratio of forward to backward amplitude varies up to 10

In Figs. (4a) and (4b) the enhancement in maximum current density is plotted for the frequencies of 10kHz and 100kHz, respectively. The enhancement is also plotted in terms of the duty cycle and the ratio of forward to backward amplitudes.
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To illustrate the overall situation of efficiency and enhancement parameters, their contours are simultaneously plotted in Figs. (5a) and (5b) for the frequencies of 10kHz and 100kHz, respectively. Constant efficiency and enhancement curves are plotted as dashed and continuous lines, respectively in each plot. It is seen that there are regions of constant enhancement, corresponding to some ‘optimal’ operation scenarios as discussed below.

There is a considerable difference between the 10kHz and 100kHz plots. It is observed that at 10kHz, the enhancement contour corresponding to $\zeta = 3$ lies well below the zero efficiency contour $\eta = 0$ in the region with negative efficiencies. Therefore, it is impossible to have a positive efficiency while having an enhancement greater than 3 at 10kHz. The unity enhancement contour $\zeta = 1$, however crosses the zero efficiency contour $\eta = 0$ for duty cycles larger than 0.6 and ratios of forward to backward amplitude under 1.5.

The situation for an excitation frequency of 100kHz is rather different. The enhancement contour corresponding to $\zeta = 10$, cross the zero efficiency contour $\eta = 0$ for duty cycles larger than 0.2 and ratio of forward to backward amplitudes under 3.1. The unity enhancement contour $\zeta = 1$ is out of the figure and not shown here. Thus, it is expected that a better optimization could take place at 100 kHz.

Now we define the dimensionless parameter $\xi$ as

$$\xi = \eta \zeta$$  \hspace{1cm} (34)
The physical meaning of $\xi$ is interesting: suppose that a prescribed waveform which has an efficiency of $\eta$ is given. According to the above discussions, its maximum instantaneous current density can be as high as $\xi i_L$. Therefore, the maximum average current which could pass through the bath would be $\eta \xi i_L$. This means that the average plating speed in comparison to the DC plating has enhanced to the amount $\xi$ which is defined in (34). Therefore, the parameter $\xi$ is a measure of enhancement in the net plating speed, being proportional to the maximum possible average current.

The enhancement in plating speed $\xi$ is plotted in Fig. (6a) and Fig. (6b) for the frequencies of 10kHz and 100kHz, respectively. The maximum values of $\xi$ for the frequencies of 10kHz and 100kHz are 2.31 and 4.56, respectively, which occur at the upper-left corner of the figures, corresponding to waveforms with large forward amplitudes and short duty cycles. In both figures, contours of negative values of $\xi$ are not shown.

![Fig. 6. Contours of constant growth in plating rate $\xi$ at (a) 10kHz; (b) 100kHz](image)

At the frequency of 10kHz, there is no specific behavior above $\xi=1$ contour. However, at the frequency of 100kHz, a second island of high plating speed develops as may be seen in the right of Fig. (6b). This island enjoys a much lower gradient in $\xi$ comparing to the island in the upper-left corner, enclosing a local maximum of 3.2, and thus has wider dimensions. This feature permits easy adjustment of waveform and therefore plating speed.

In conclusion, it is possible to obtain a considerably faster deposition rate by pulse-periodic-reverse electroplating through proper selection of duty cycle and ratio of forward to backward current waveforms. The waveform of the input current together its frequency, determines the enhancement in the net plating speed. The net plating speed can thus be optimized by choosing proper duty cycle and ratio of forward to backward amplitudes.

7. CONCLUSIONS

A detailed theory of carrier distribution in electrolytic cells has been derived for prescribed waveform shapes and frequencies. Laplace transformations were used to solve a one-dimensional time-dependent diffusion model with linearized electrochemical boundary conditions. The results for steady state, biased sinusoidal, and arbitrarily shaped rectangular waveforms have been derived. Optimal waveforms were shown to exist in electroplating process, at which the maximum current density is enhanced while maintaining a high level of efficiency, therefore obtaining a faster deposition rate comparing to DC conditions. Numerical results have been obtained for the acid-copper bath. In future, necessary electronic circuits will be developed to verify the results experimentally.
REFERENCES