

Pulsed electrodeposition of zinc in magnetic fields: diffusion layer relaxation followed by laser interferometry

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The pulsed galvanostatic deposition of zinc was carried out in the presence and absence of an externally applied magnetic field of 0.43 T. The concentration time profiles and the relaxation of the cathodic diffusion layer during the pulsing sequence have been determined by using laser interferometry. When, in the pulsing mode, longer 'off' periods compared to the 'on' periods were used, significantly greater relaxation of the diffusion layer was observed. The fringe shift time profiles for the electrodes kept in the vertical or anode over cathode positions are influenced by the hydrodynamic effect; the magnetic field effect on the relaxation of the diffusion layer has been observed. The electrodeposited Zn has been analysed by scanning electron microscopy; the Zn deposit obtained by pulsed current electrolysis in the cathode over anode position is dense and uniform.

1. Introduction

The galvanostatic deposition of zinc has been investigated in the past with the major objective of obtaining uniform and adherent deposits of zinc [1-5] as these deposits find use in light weight Ag-Zn batteries. To achieve this objective, suggestions such as an impinging flow of electrolyte [4], increasing the concentration of Zn^{2+} or decreasing the electrolytic current [1, 2] have been proposed. All these methods are based on the principle of limiting the diffusion layer growth to maintain a higher concentration of Zn^{2+} near the electrode surface. In d.c. electrolysis (galvanostatic deposition), the growth of the diffusion layer would limit the supply of the electroactive ion to the electrode; this limitation is removed in experimental situations by convective diffusion or forced transport of the electroactive material. One other way to overcome this problem of the growth of the diffusion layer would be to periodically destroy part of the diffusion layer so that the local concentration of Zn^{2+} can be enhanced. This objective has been achieved by pulsing the current during the deposition of gold [6]. Several theories have been proposed for obtaining values of the surface concentrations during pulsed depositions [6, 7, 8]. To evaluate these theories and the models used, the diffusion layer thickness must be known. Only measurements of the thickness by indirect methods such as the rotating disc are available [6].

A previous paper from our laboratories [9, 10] reported the galvanostatic deposition of Zn and the effect of added paramagnetic ions on its deposition. In

this work we examined pulsed galvanostatic deposition of Zn through laser interferometry. This technique allows the direct visualization and measurement of the growth of the diffusion layer. We have examined in this study the course of the diffusion layer growth and its relaxation in pulsed electrolysis. Two types of experiments were conducted: with current passing for a selected time and open circuit for a selected time — this sequence is continuous and called the current on-off sequence. In the other type of pulsed electrolysis, the current is initially followed by reversal of the current direction; this sequence is called the polarity reversal sequence.

We reported earlier the effect of magnetic fields on d.c. deposition of Zn [9]. The effect was demonstrated in the vertical position of the electrode where natural convection occurred during electrolysis. The magnetic field enhanced the electrohydrodynamic effect. This work is on the effect of a magnetic field on pulsed deposition in the cell Zn/ZnSO₄/Zn. The morphology of the Zn deposits obtained has been examined by SEM. Remarkably uniform deposits result in the C/A position while pulsing the current in the magnetic field.

2. Experimental details

The pulsed galvanostatic deposition of Zn was carried out in a laser interferometric cell. The electrodes were formed by cutting a centre slice from a circular disc of 4.30 cm radius. The long side of the electrode was polished with emery paper and acid etched before

fitting into the cell. The entire disc was covered with glyptol (insulating spray) except for the long side which was the only active part on the electrode surface. The gap between the plane parallel electrodes in the interferometer was 2.50 mm.

The cell was placed in a brass cell holder; the optical glass flats were placed on either side of the electrodes and clamped in the cell holder. A He-Ne gas laser (1 mW) was the light source for the interferometer. The methodology adopted for recording the interferograms has been described earlier [10-13]. The fringe movements were videotaped on a Hitachi video recorder (VTR model VT-7A) and were displayed on a 20" Hitachi colour television at about 30X magnification. An RCA CC030 microprocessor controlled camera was used to follow the fringes.

The pulsed deposition of Zn was carried out using a Keithley constant current source (Model 220) by manually switching the current to on-off positions or to the polarity reversal position. The cell voltages were followed using a digital multimeter.

The refractive index of the ZnSO_4 (BDH) solutions were measured using a Bausch and Lomb precision Abbe refractometer thermostated at 25°C. SEM recordings were done using a Jeol (Japanese Engineering Optics Ltd) instrument. The magnetic field effect experiments were conducted by placing the interferometric cell between the pole pieces of the magnet. The set-up contained no magnetic material. The strength of the magnetic field was varied by adjusting the current passing through the magnet coils. The coils were water cooled to maintain constant field strength. The magnetic field was measured using a digital gaussmeter.

3. Results and discussion

The pulsed deposition of Zn was carried out in the present investigations with vertical electrodes (V-position) or with the cathode placed over the anode (C/A). The current densities used in the experiments were either 0.59 mA cm^{-2} (corresponding to $i = 0.50 \text{ mA}$) or 1.00 mA cm^{-2} (corresponding to $i = 0.84 \text{ mA}$). A typical set of measurements from laser interferometric recordings during the pulsed electro-deposition of Zn in the V-position is shown in Fig. 1. After 30 s of electrolysis, the fringes at the cathode and anode shift smoothly as shown in Fig. 1(a) due to depletion of zinc at the cathode causing a lowering of the solution refractive index; at the anode, the dissolution of zinc produces a higher refractive index thereby causing the fringes to bend in the opposite direction (relative to the cathode).

As the current is interrupted at the end of the 30 s, the fringes at the cathode and anode tend to relax as the refractive index changes continuously due to continued convective mixing of the solutions and this process is shown in plot (b). If the sequence of current on and off is maintained, the fringes build up and relax corresponding to the growth and decay of the diffusion layers at the two electrodes.

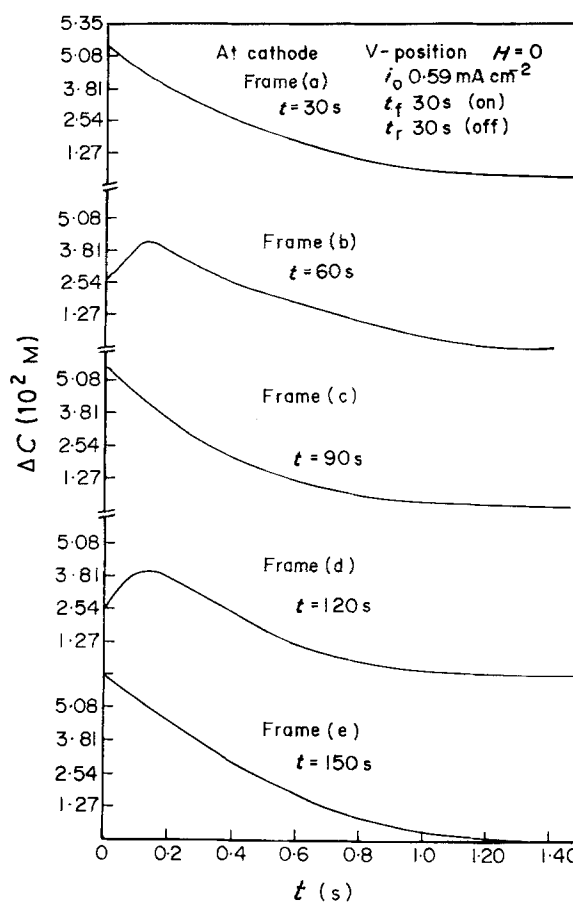


Fig. 1. Measurements of fringe shifts from interferograms obtained during pulsed electrolysis of 0.1 M ZnSO_4 using Zn anode and Zn cathode with a c.d. of 0.59 mA cm^{-2} . The x-axis is magnified 18 times. The time pulsing sequence is 30 s on with 30 s off. The measurements made at various times during the pulsed electrolysis are indicated on the curves. The electrode separation distance is 3 mm in the vertical position.

The fringe shift (bend) implies that the refractive index (concentration) in the diffusion layer is different from that in the bulk of the solution. By measuring the fringe shifts during the above pulsing sequence of 30 s on and 30 s off we can construct a fringe shift against time behaviour. Note that one fringe shift corresponds to a concentration change of $3.18 \times 10^{-3} \text{ M}$ (obtained from the refractive index against concentration of ZnSO_4 plot).

A typical plot of maximum fringe shift (ΔF_{max}) against time is shown in Fig. 2a which also shows the corresponding changes in the cell voltage during the pulsing sequence. The fringe shift at the anode is less than at the cathode due possibly to differences in the local fluid flow natural convection and/or the zinc hydroxide-zincate equilibrium. The shape of the decay curve shown in Fig. 1 was obtained from the profiles observed on the video monitor during the actual experimental run. The fringe shift does not reach the background level during the current-off period indicating the relaxation of the diffusion layer is not complete. Some decrease in concentration at the cathode (increase at the anode) remains until the next on-off sequence begins. We then come to an important conclusion that the time required for forming the diffusion layer and the time for its destruction are not

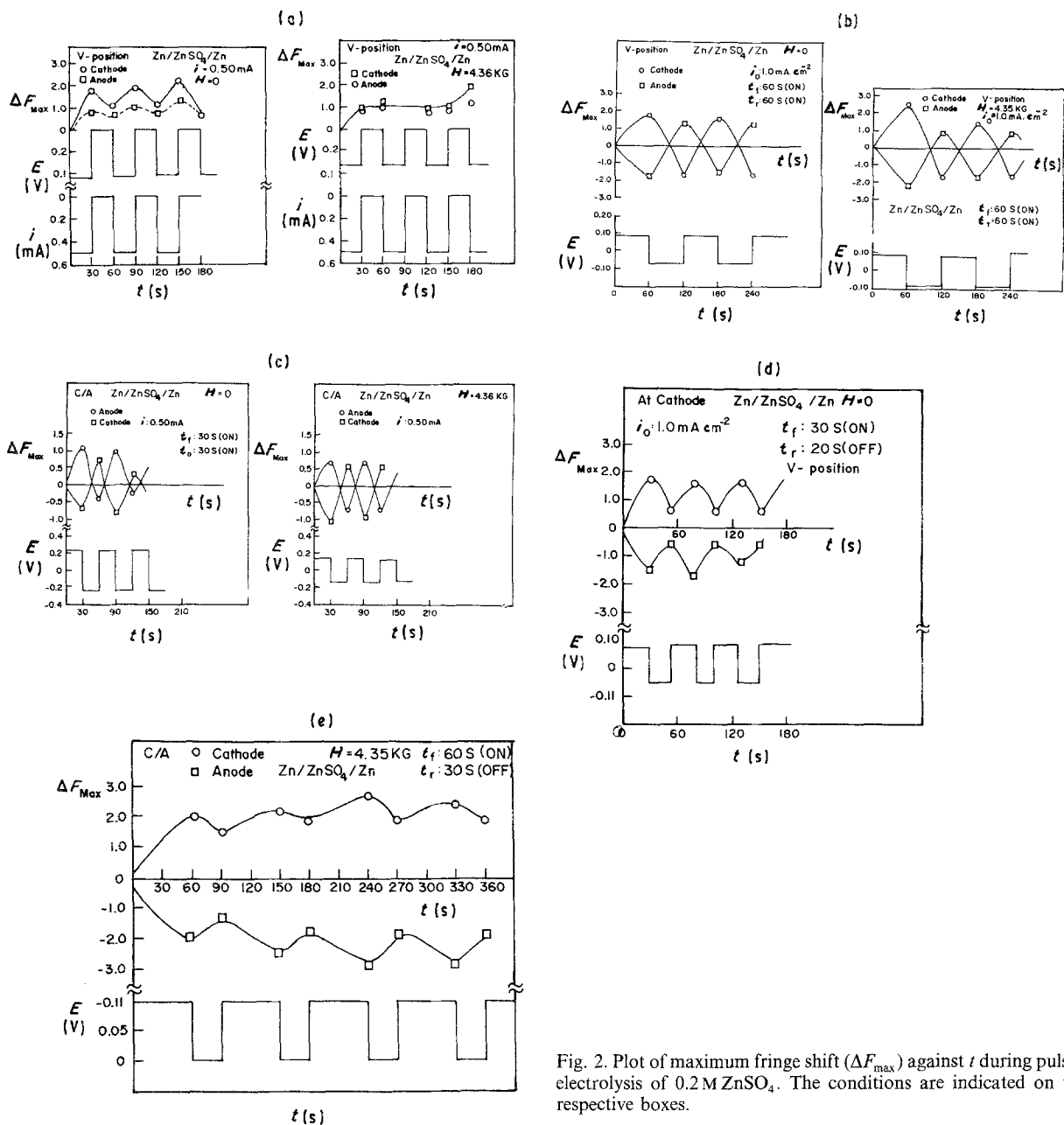


Fig. 2. Plot of maximum fringe shift (ΔF_{max}) against t during pulsed electrolysis of 0.2 M ZnSO_4 . The conditions are indicated on the respective boxes.

identical. In the formation of the diffusion layer both migration and diffusion are involved. During relaxations (open circuit) only diffusion operates. Furthermore, in spite of the existence of the remaining diffusion layer, its growth and attainment of the maximum fringe shifts during the next current pulse are not changed. In other words, the value of the maximum fringe shift throughout the succeeding current-on periods was nearly the same. This point will be further discussed in the later section on the thickness of diffusion layers. Experiments were performed by reducing the current-off period from 30 s to smaller values to examine the effect on the maximum fringe shift during electrolysis. When the current-off period was either 5 s or 10 s, there was no easily measurable change of the fringe shift. However, this does not mean the layers close to the electrodes (up to 0.05 mm) have not relaxed, but relaxation appears to be slow initially. When the current-off period is beyond 20 s, a tenth of a fringe shift of relaxation occurs, which is

significant and measurable. For comparison to a 30 s current-off period, we have included a recording (Fig. 2) of the fringe shift – time plot for 30 s current on and 20 s current off pulsing sequence. The pulsing sequences used in the experiments are also shown in Fig. 2d.

For the current research experiments, pulsing introduces changes in interferometric profiles as shown in Fig. 2b. In an experiment with current on for 60 s and current reversal for 60 s, the fringe shifts at the cathode and anode show reversal of the directions after the switching, rather than just the diffusion layer relaxation seen in Fig. 1. This results in slightly smaller fringe shifts in the alternating periods of the experiment suggesting the structural role of the diffusion layers in deposits, i.e. convective-mixing of electrolytes at the electrodes. This trend was also observed with 30 s current on and 20 s current reversal period even at the lower current density of 0.59 mA cm^{-2} .

The C/A electrolysis follows a pattern similar to

that observed with the V-position. Figure 2e shows the maximum fringe shift against time during a 60 s on and 30 s current off sequence. The fringes show an oscillatory pattern with the fringe shift maximum reaching a constant value. This plot also shows the cell voltage variation during the current pulsing (see Fig. 2a-d). Note even in this configuration the diffusion layer does not relax back during the off period and yet the fringes do reach the same maximum value during the subsequent current-on period. Thus the transport of the Zn^{2+} ion to the electrode reaches the same original value even when the solution is partly disturbed. C/A positioning of the electrodes switches the orientation from C/A to A/C during the pulsing sequence. The instability of the medium, i.e. on-set of convection arising from heavier solution at the top electrode (anode momentarily) due to Zn dissolution and the solution at the bottom of the cell becoming lighter due to Zn^{2+} reduction at the cathode, has been well substantiated in several previous results [14-17]. Thus during the pulsing sequence, one should expect microturbulence to occur during this electrolysis.

The current pulsing of 30 s on with reversal of polarity for 30 s, during electrolysis of $ZnSO_4$, generates fringes which periodically change the direction of the shift for reasons discussed earlier (see Fig. 2c). However, in this sequence, one tends to generate microturbulence at reversal of polarity to the A/C configuration. But the original fringe shifts are reached

during cycling when the electrode reaches its initial polarity. The cell voltage oscillates from about 0.20 V to -0.20 V during pulsing. Due to a small uncorrected potential drop in the cell, the cell voltages vary slightly from one run to the next, nevertheless, the pattern of oscillations does not change.

3.1. Magnetic field effect on pulsed deposition

The magnetic field has been shown to influence the laser interferometric electrolysis fringes conducted in the V- and A/C position [10, 13] due to the electrohydrodynamic effect on the fluid. This results in the generation of wavy patterns in the interferograms of electrolysis of $ZnSO_4$ at Zn electrodes. Pulsed electrolysis of $ZnSO_4$ with the current on for 30 s and off for 30 s, has generated a fringe shift-time pattern as shown in Fig. 2a with and without a 0.436 T field. The diffusion layer relaxation appears to have been slowed down by the field to the extent of giving an apparent effect on constant fringe shift during this electrolysis. It should also be noted that the fringe shift values in the magnetic field are less when compared to the zero field values due to the hydrodynamic effect operating in the cell. When the current reversal pulsing is performed in the magnetic field, the fringe shifts during 30 s current on with 30 s current polarity reversal reach nearly identical values (see Figs 2a and c). Approximately 40% less applied potential was required, as expected [13] and shown in panels a to c, for the same current density at 0.435 T or 4.35 kG.

3.2. Diffusion layer relaxation

From the laser interferograms obtained during the electrolysis of $ZnSO_4$, the diffusion layer thicknesses were measured and are plotted as a function of time in Fig. 3. The layer growth during the d.c. electrolysis (Fig. 3a) proceeds continuously under C/A conditions, and these separations of electrodes, until the conditions of semi-infinite diffusion are breached. The surface concentration of the metal ion in relation to the diffusion layer thickness has been derived earlier [8] as

$$\frac{(C_1 - C_0) * nFD}{i_{dc} \delta} = 1 - \frac{8}{\pi^2} \sum_{j=1}^{\infty} \frac{\exp[-(2j-1)^2 at]}{(2j-1)^2} \quad (1)$$

where C_1 refers to the surface concentrations, C_0^* is the bulk concentration of Zn^{2+} , n is the number of electrons transferred, F is the Faraday number, D is the diffusion coefficient of the ion, i_{dc} is the current density, δ is the thickness of the diffusion layer, a is defined as $(\pi^2 D/4\delta^2)$ and t is the time elapsed during the electrolysis. From this expression, the diffusion layer thickness is predicted to be an exponential function of time if there is no limiting process operating such as convection or a chemical reaction. The pulsing experiment performed did not eliminate the effects of migration and convection, so application of Equation 1 must be approached with caution.

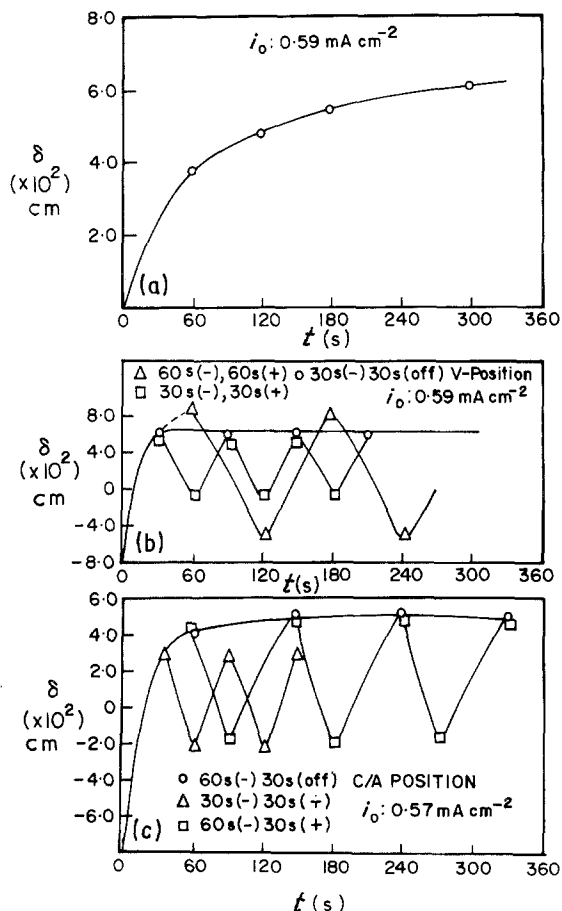


Fig. 3. The growth of the cathodic diffusion layer δ during: (a) d.c. electrolysis, (b) pulsed electrolysis in the V-position and (c) pulsed electrolysis in the C/A position of 0.1 M $ZnSO_4$. Experimental conditions are indicated in the respective boxes.

The diffusion layer thickness used by Rosebrugh and Miller was one half of the separation of the electrode, which is correct in theory. Tobias *et al.* [18] have summarized this and other work in the field, giving more practical methods of calculation of δ in the usual electrochemical transport circumstances. The specific case for current reversal has also been solved by Forgacs *et al.* [19].

Remembering that migration and convection are present (as previously mentioned) it should nevertheless be possible to make some valid suggestions from the results shown in Fig. 3. In the C/A position Equation 1 need only be modified for migration, which is usually done by multiplying the left side by the transport number of the inactive ion, here SO_4^{2-} as $(1 - t_+)$. Figure 3a shows the continuous approximately exponential growth predicted in the C/A position. Pulsing at 30 s on, 30 s off or 60 s on 30 s off produced a nearly constant value of the diffusion layer. It should be noted that convective effects limit the growth of the diffusion layer at any height in a vertical electrode but the diffusion layer has been shown to increase with height, that is, it is thicker near the top at the cathode [20]. The present electrode and cell were not very deep and measurements were made at a constant height and over less than one half of the electrode height and then averaged to compensate for the thickening effect. We believe that no such thickening occurs when the electrochemical magnetohydro-magnetic effect is operating.

Figure 3b at 0.59 mA cm^{-2} in the V-position shows three pulsing modes for comparison. Each mode has equal time either in the on-off or on-reversed mode. The reversal mode at 30 s shows a reduction of δ to zero and the 60 s sequence has almost twice the amplitude of oscillation in contrast to the 30 s on off sequence which produces a nearly constant δ .

Figure 3c is for the C/A experiment, which is similar to the V-position. The 60 s on with 30 s reversed gives the greatest oscillatory amplitude, indicating that this mode, or one similar to it, should give the lowest resistance (thinnest average, least resistive, diffusion layer) deposition conditions. It seems likely that full scale deposition baths with deeper electrodes may cause some variation in these recommended conditions.

3.3. SEM recordings

SEM recordings of the Zn cathode in the electrolysis of ZnSO_4 show morphological differences in the

pulsed depositions in the V- and C/A positions. The V-positions generate coarse and uneven deposits of Zn. The morphology of the Zn deposits produced in the C/A position tend to be fractal but this position does not give a uniform deposit. In pulsed deposition, C/A switches to A/C periodically. Microturbulence is generated with polarity reversal which gives an even deposit, especially under the influence of the magnetic field, when electrochemically induced flows (forced convection) reinforce the natural convection.

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