



The William Blum Lectures

#04 - Abner Brenner - 1962



**The 4th William Blum Lecture
Presented at the 49th AES Annual Convention in Milwaukee, Wisconsin,
June 24, 1962**

**The Speed of Processes Involved in Electroplating:
Movement of Solute, Attainment of
the Steady State and Formation of Metal**

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Recipient of the 1961 AES Scientific Achievement Award





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Editor's Note: Originally published as A. Brenner, *Annual Technical Proceedings of the American Electroplater's Society*, 49, 9-13 (1962), this article is a re-publication of the 4th William Blum Lecture, presented at the 49th AES Annual Convention in Milwaukee, Wisconsin, on June 24, 1962. When this lecture was delivered, a short movie was used by Dr. Brenner to illustrate galvanostametry. The movie is lost to history, but the text is descriptive in and of itself. Indeed what is published here is all that was published in the 49th Annual Technical Proceedings. While we regret that we cannot provide the reader with the complete record, we hope that the information will speak for Dr. Brenner.

The closing of a circuit on a plating tank results in the deposition of metal in a very short period of time, as anyone can verify by examining the cathode a few seconds later. In addition to the deposition of metal itself, the plating process involves a number of auxiliary phenomena in which time plays a role. The most familiar of these are the phenomena of convection, diffusion and electrical migration which are the agencies responsible for the transport of metal ion into the cathode diffusion layer. These agencies make possible the continuous operation of a plating process. They are collectively referred to as mass transport.

Knowledge concerning the element of time involved in the various phenomena associated with electrodeposition is useful for both academic and practicable purposes. However, this subject has not received much attention from the electroplating profession. The phenomena associated with mass transport have received a considerable amount of study by electrochemists and hydrodynamicists, but the time involved in the demonstrable appearance of metal after a switch is thrown has not been extensively investigated.

The purpose of this lecture is to discuss in a popular or descriptive manner the element of time involved in the various phenomena associated with electrodeposition. It includes a brief review of information already available in the literature and concludes with a summary of some experiments which are now in progress at the National Bureau of Standards [*now NIST - Ed.*].

The most obvious thought pertaining to the element of time in electrodeposition concerns the rapidity with which metal appears on the cathode after the switch is thrown. This subject is the most interesting one pertaining to the time element, but unfortunately also the most difficult one upon which to obtain information. There is little on this subject in the literature. For that reason, this subject is treated last, and the time element involved in the better known processes of mass transport is discussed first.

The aspect of mass transport that will be taken up now is the average speed at which metal ions must move toward the cathode in a continuous plating process. An approximate calculation is readily made in the following manner. Consider a plating bath that contains 1 equivalent of metal ion per liter, and let the liter of plating solution be contained in a cube with sides of 1.0 dm. The cathode is flat against one side of the cube and has an area of 1.0 dm² as shown in Fig. 1. A current of one ampere passed through the system for one second constitutes one coulomb of electricity or approximately one-hundred thousandth of a Faraday. To supply this amount of metal, one can visualize that the metal ions in the cube of solution (which contains one equivalent of metal) must have advanced one-hundred thousandth of a decimeter toward the cathode. This is schematically represented in the figure by a slice of the bath. The average rate of movement of ions per second, therefore, must be approximately 10⁻⁵ dm/sec or about 0.04 mil per second. This distance is about equivalent to the thickness of the chromium deposit that is currently recommended for decorative coatings.

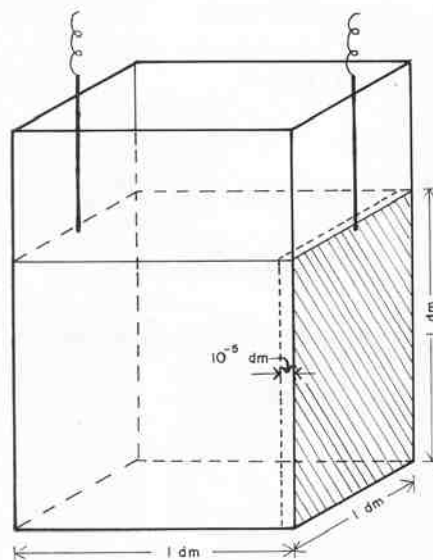


Figure 1 - Diagrammatic representation of the average rate of movement of ions in one second with a current of 1.0 A/dm^2 . For pedagogic purposes, the current is considered to be applied to a cathode immersed in a bath, 1.0 dm on a side, containing one equivalent of metal ion. The passage of one coulomb requires that on the average a metal ion in a slice of the bath 10^{-5} dm thick must have moved up the cathode.

This rate of movement of ions could also have been approximately calculated from the electrical mobility of ions, which is of the order of $5 \times 10^{-5} \text{ dm}$ per second for unit voltage drop per cm. Since the voltage drop in the plating bath would be somewhere between one-fifth and one-tenth of a volt per cm this gives a value near the one hundred thousandth of a decimeter, as previously obtained.

The mass transport represented by this movement of ions is to be considered as the average rate at which the ions move across the cathode-solution interface under the influence of electrical migration and diffusion. In a plating bath containing no added conducting salts, diffusion supplies usually a little over half of the metal ion. In a bath containing much hydrogen ion, diffusion may supply as much as 90% of the metal ion.

Convection is not considered to supply metal ion directly to the cathode, since the solution at the interface is considered to be at rest, but it does supply metal ion to the cathode diffusion layer, which has a thickness of about one-third millimeter or a few hundredths of an inch. Convection currents are caused by the difference in the density of the depleted solution in the cathode diffusion layer and the more concentrated solution in the body of the bath. This causes a pattern of convection currents, which in some locations flow vertically upwards and in others obliquely toward the cathode. For the purpose of understanding the velocity of these convection currents, it is convenient to consider the currents as resolved into a vertical component and a horizontal component normal to the cathode.

The velocity of the upward convection current has been observed directly by Ibl and Müller¹ who suspended a fine powder of colophonium in the plating bath and observed the motion of the particles with a microscope. Some of their data are presented in Fig. 2 which shows the velocity profiles of convection currents along a plane vertical cathode at a distance of about 70 mm above the bottom edge. The maximum velocity for a plating rate of 0.3 A/dm^2 was about 1.0 mm/sec . The velocity increased with the current density, which is to be expected, since the depletion of metal ion becomes greater with current density. Also, it will be noted that the velocity of the convection current was zero at the cathode-solution interface, because of the adhesion between the liquid and the cathode, and increased with distance, reaching a maximum at about one-third millimeter from the cathode. This is understandable, since at about 1.0 mm from the cathode the depletion of metal ion becomes negligible; hence, the driving force for the convection current also disappears.

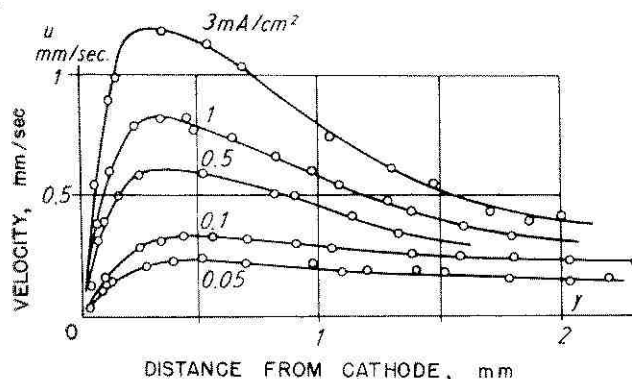


Figure 2 - Variation with current density of the velocity profiles of the vertical convection currents along a cathode. The velocity profiles are for a height of 70 mm above the bottom edge of a plane vertical cathode. Current densities are indicated by the numbers on the curves. Reproduced from Ibl and Müller.¹

These convection currents start to develop as soon as plating begins. Because it takes time for the differences in density of solution to develop and time to set a mass of liquid in motion, velocities gradually increase during the first two minutes of plating. Figure 3 shows that the vertical velocity of the bath along a cathode was only a few tenths of a millimeter per second about one half minute after the circuit was closed, and about two minutes were required for the velocity to come up to its steady value. Thus, in a strike plating operation of short duration the role of convection in replenishing the solution is not important.

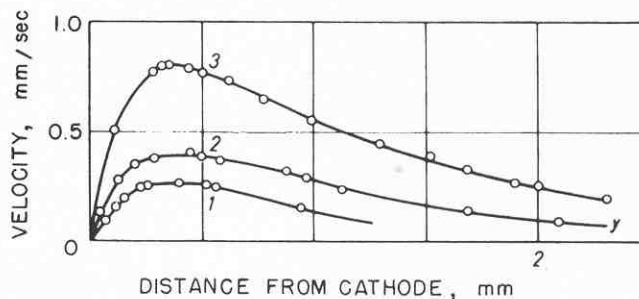


Figure 3 - Variation of the velocity profiles of vertical convection currents along a cathode with the time after closing of the circuit. The height of the observation point was 70 mm above the bottom of the plane vertical cathode. Current density, 0.1 A/dm². Curves 1, 2 and 3 represent, respectively, 0.5, 1.0 and 2.0 minutes after the beginning of electrolysis. Reproduced from Ibl and Müller.¹

The convection currents that move upwards parallel to the cathode do not supply much metal ion to the cathode diffusion layer because they are already depleted. The component of the convective flow that supplies metal to the diffusion layer is the component that is perpendicular to the cathode. I have no experimental data on the velocity of this flow. A calculation made using the equations of Keulegan³ for a plating process operating at a current density of about 4.0 A/dm² gave a velocity of about 3×10^{-4} cm/sec or 0.1 mil/sec. It may be noted that this velocity of flow is very low and of about the same order of magnitude as the mass transport calculated in the first part of this paper. This is understandable, since convection must restore to the outer boundary of the cathode diffusion layer the metal ion that is transported to the cathode-solution interface by diffusion.

The next subject to consider is the time required for a plating process to reach a steady state. The latter phrase means that the concentration profile within the cathode diffusion layer does not change with time. When the circuit is first closed and plating begins, the metal ion adjacent to the cathode is first deposited, thus impoverishing the diffusion layer. The degree of the impoverishment increases with time; also, the region of impoverishment spreads further from the cathode. After a period of about two minutes these changes in the concentration of the diffusion layer cease and the concentrations remain sensibly constant from then on. The rate at which the depletion of metal at the cathode-solution interface reaches the steady state is

#04 - Abner Brenner - 1962

shown in Fig. 4 for a nickel plating solution. After about 30 seconds, about half of the complete change has occurred. After the current is turned off, the concentration of metal ion near the cathode begins to build up again at a slightly slower rate than that required to reach the steady state.

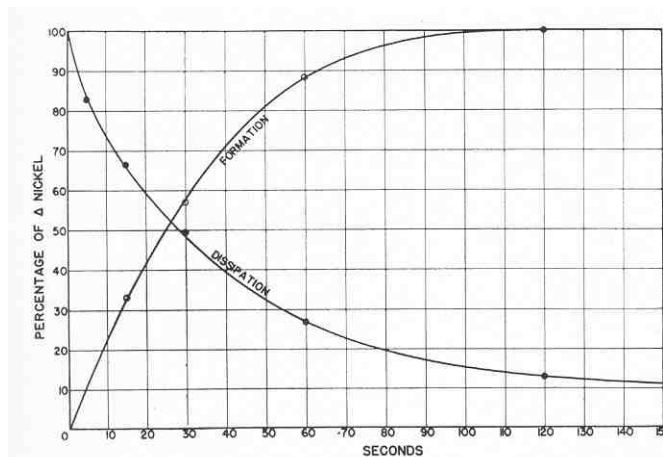


Figure 4 - Rate of formation and dissipation of the cathode diffusion layer in a 1.0M nickel plating bath as indicated by the relative variation in the depletion of nickel ion. Current density, 2.0 A/dm². Depletion of nickel at the cathode-solution interface, 0.27M or 27%. Data of Brenner.²

Most plating baths, either practically or theoretically, possess a limiting current density for the continuous operation of the process without production of burnt deposits. Current density in excess of the limiting value goes into the initiation of another electrode reaction, such as the discharge of hydrogen. At the limiting current density the concentration of metal ion at the cathode-solution interface is reduced virtually to zero. Under this condition, diffusion carries metal ion to the interface at the greatest rate of which it is capable.

The electrodepositor is familiar with the use of strikes by means of which a much higher current density than the limiting current density can be passed for a short period of time without producing burnt deposits. This is possible because in a short period of time the metal ion concentration is not reduced to zero. The larger the applied current density, the shorter is the time that it can be applied without causing hydrogen evolution and the formation of a rough deposit. The theory of diffusion provides us with an approximate relation between the current density and the period that the current can be applied:

$$I^2 = \frac{k}{t}$$

This states that the square of the current is inversely proportional to the time. For example, if it were possible to apply a current of 10 amperes for one second on an object in a particular bath, it would be possible to apply a current of $10\sqrt{2}$ or 14 amperes for one half second or a current of $10\sqrt{3}$ or about 17 amperes for one third second. Thus, the current that can be used for a strike rapidly increases as the period of its application is reduced.

Experimental demonstrations of this relation have been described in the literature. Figure 5 shows some data that we obtained for the oxidation of iodide ion to iodine at an anode. The reason that we used this reaction rather than metal deposition was that no solid product formed at the electrode (the iodine remained in solution); hence the area of the electrode did not change during the experiment.

These data were obtained by a new technique which I shall describe briefly. In making a study with a strike current, there must be some means of determining the moment that the reaction under consideration has reached its limiting rate and hydrogen or oxygen begins to discharge. Usually this is done by observing a sudden change in the voltage. In the new technique the end point of the time is indicated by the dropping of a column of electrolyte which was suspended in an evacuated glass tube.

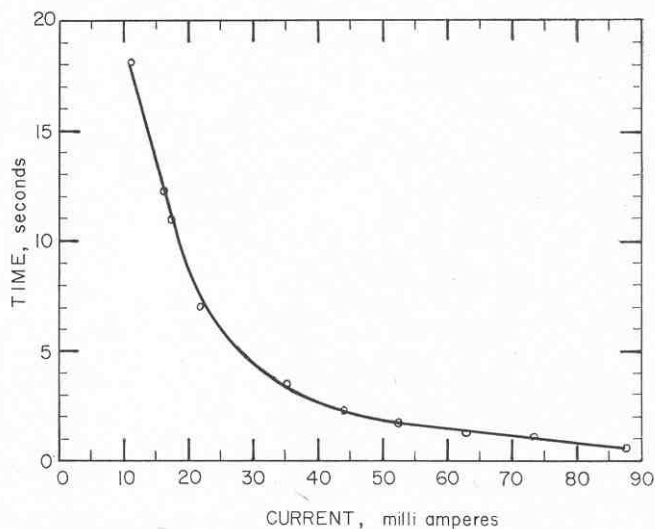


Figure 5 - Inverse relation between the applied current density and the time required for the limiting current density to be exceeded in the anodic formation of iodine from iodide ion. Solution contained about one percent of sulfuric acid. Limiting current density determined by galvanostametry. The data approximately fits the equation:

$$I^2 = \frac{k}{t}$$

where I is the current density, t is the time and k is a proportionality constant.

This new technique has been given the name of galvanostametry, derived from the Greek word *stalao*, meaning to drop. It was reported by John Sligh, a member of the Metal Deposition Section, at the May [1962] meeting of the Electrochemical Society.

The procedure involves the suspension of a column of electrolyte in a long tube, which is attached to an evacuated bulb. The liquid is in a metastable condition, being under tension. Two electrodes are provided at the top of the column, and current is passed between them. Typical apparatus are shown in Figs. 6 and 7. Whenever the electrode reaction leads to the formation of the most minute amount of gas on an electrode, the gas nucleus causes the column of electrolyte to drop suddenly. The amount of gas on the electrode need be only of the order of a monomolecular layer. Thus the procedure has value as a sensitive indicator for electrochemical reactions, for example, for indicating when the limiting current density of a plating process is exceeded, or for indicating the decomposition potential of water.

The galvanostametric procedure is illustrated in a short two-minute movie showing a measurement of the decomposition potential of water. An acidulated solution is used which is colored red to make observation easier. In the movie you see the manner in which the tube is filled. The tube is under vacuum, so that the water column is not sustained by air pressure. The column must be thought of as actually being supported by adhesion to the top of the glass vessel and to be under tension. You will note that the voltage between the electrodes is gradually increased. The column suddenly drops at the voltage for the decomposition of water which is about 1.7 V. The experiment is repeated with a close-up which shows the face of the voltmeter and the electrodes with greater clarity.

Finally we come to the most interesting aspect of the time element in electrodeposition; this is the time required for a palpable deposit to appear after the circuit is closed. There is very little tangible information on this subject in the literature, but there is much speculation about various intermediate processes which are assumed to be slower than the final step of metal deposition. Recently, my section at the Bureau has become interested in this matter and has done some preliminary experiments directed toward obtaining some qualitative ideas of the rate at which an electrode reaction occurs after the circuit is closed.

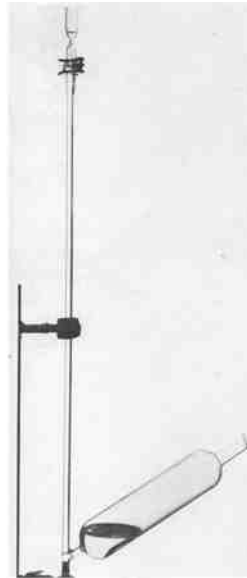


Figure 6 - Apparatus for galvanostametry, comprising an evacuated system containing a suspended column of water and two electrodes sealed in the top of the column.

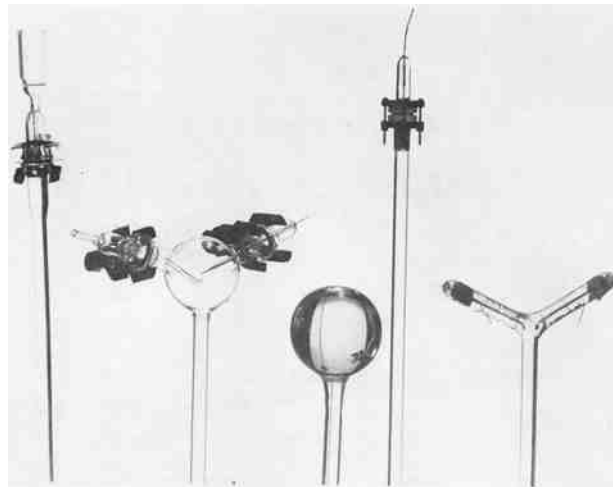


Figure 7 - Various designs of tops of columns used for suspending an electrolyte in the use of galvanostametry. The most versatile types of equipment are those with a demountable top or tubulure which permits the ready introduction of various types of electrodes.

In one set of experiments, Vernon A. Lamb used a pulse generator to apply short pulses of current of about one to ten microseconds duration to an electrolytic process. In order to obtain enough product to be visible, the current density had to be very large. Since the current which could be delivered by the pulse generator was limited to about 0.1 ampere, it was necessary to use a very small cathode, for example, the cross section of a wire a few mils in diameter. The current density on this small area may have been of the order of a million amperes per dm^2 , but it lasted only for a period of microseconds. With this procedure Lamb observed that microsecond pulses of current actually produced enough product at the electrode to be seen. In particular, a deposit of copper with dendrites which were visible under a microscope was obtained in a microsecond.

These experiments are still in progress and a complete account will be published later. They show that a charge of electricity is rapidly taken up by the system, but they do not tell how fast the product is formed. It may have formed during the passage of current or it may have been formed a fraction of a second later.

#04 - Abner Brenner - 1962

Finally I wish to report on a preliminary experiment which throws light on the rapidity of an electrode reaction. The experiment was made by galvanostametry with solutions of dilute acid. The passage of current between the electrodes resulted in the production of oxygen and hydrogen at the electrodes, thus causing the column to drop, as shown in the movie. The purpose of the experiment was to determine how rapidly the gas formed at the electrode.

Exploratory experiments with alternating current showed that for low currents the column did not fall. This indicated that the effect of the forward and backward pulses of current annulled each other. However, with a current above a certain critical value the column fell. This current roughly corresponded to an amplitude such that a single directional pulse produced a layer of gas on the electrode. This indicated that once a gas film had formed on the electrode surface the column broke away sufficiently to prevent the reverse reaction from occurring. On the basis of these observations with alternating current, we considered that the time involved in the formation of the gas film could be studied by using two separate pulses of current.

The experimental procedure was simple. First a pulse of current which lasted for only five microseconds was applied to the electrode making it cathodic. Then immediately following, a second pulse of current was applied in the opposite direction for ten microseconds. This was equivalent to the passage of one complete cycle of a square wave alternating current. The passage of the pulses was made visible on an oscilloscope. The charge of current in either pulse was sufficient to drop the column. If the formation of gas were slow, then reversal of current in the second pulse would remove the effects of the first pulse and the column should remain suspended. However, if the reaction involving the formation of gas were complete, then the second charge of current in the reverse direction might not remove it with sufficient completeness to prevent the column from dropping.

In this experiment the column dropped despite the immediate application of the reverse pulse of current. This result demonstrates, in my opinion, that the electrochemical reaction must have occurred within a period of five or ten microseconds. With more elaborate instrumentation perhaps we can investigate these phenomena for still shorter periods of time. However, these preliminary experiments have convinced me that electrochemical reactions are very rapid and that they perhaps occur instantaneously with the passage of current.

References

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3. G.H. Keulegan, *J. Research Natl. Bur. Std.*, **47**, 156 (1951).

About Dr. Abner Brenner (from the biography printed in 1961 at the time of his receiving the AES Scientific Achievement Award)



Dr. Abner Brenner was born August 5, 1908 and received his B.A. degree in 1929 from the University of Missouri, M.S. degree from the University of Wisconsin in 1930 and Ph.D. from the University of Maryland in 1939. He has been on the staff of the National Bureau of Standards since 1930. Some of the subjects on which he has done research are alloy deposition, physical properties of electrodeposits, electroless plating, electrodeposition of metals from Non-aqueous media, cathode diffusion layers, thickness gauges for electrodeposits and deposition of metals from the vapor phase.

He "as been Chief of the Electrodeposition Section for about the past ten years. During this time the activities of the Section have broadened to include other fields as well as conventional electroplating. The work of the Section, on the one hand, deals broadly with metal coatings obtained by electrodeposition from aqueous, organic or fused salt media, or by deposition from the vapor phase. On the other hand, the Section does fundamental work on the mechanism of electrolytic processes which do not necessarily involve metal deposition.

He has served on the Editorial Board of Plating, and on several committees of the AES. He has been active in the Electrochemical Society, being the divisional editor for electrodeposition from 1950 to 1958 and a past chairman of the Electrodeposition Division. He is a member of the Institute of Metal Finishing (England) and received from the Institute the Hothersall Medal in 1961. He is also a member of the American Chemical Society and the Washington Academy of Sciences.