The 26th William Blum Lecture
Presented at the 72nd AES Annual Convention (SUR/FIN 1985)
in Detroit, Michigan
July 15, 1985

Electroanalytical Methods for Research and Development in Electroplating

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Editor's Note: Originally published as *Plating & Surface Finishing*, 72 (10), 34-43 (1985), this article is re-publication of the 26th William Blum Lecture, presented at the 72nd AES Annual Convention, SUR/FIN 1985, in Detroit, Michigan on July 15, 1985. On a historical note, SUR/FIN 1985 was the last conference under the AES banner. By the time this lecture was published, the name change to the American Electroplaters and Surface Finishers Society (AESFS) had taken place, although the acronym would soon be shortened to the more familiar AESF.

Introduction

Advances in the technology of electroplating and other finishing techniques have been made by the application of basic principles and knowledge in many traditional disciplines of science and engineering. These include physics, chemistry, electrochemistry, materials science, metallurgy, and electrochemical, mechanical and electronics engineering. Each investigator comes with a background in a different area and contributes to the progress of one or more aspects of the technology.

I came to this field with experience primarily in electroanalytical chemistry acquired during many years of association with Professor Izaak M. Kolthoff, an eminent analytical chemist and great educator at the University of Minnesota. Upon joining Bell Laboratories, I had many opportunities to utilize this experience and to learn about the usefulness of electroanalytical methods for many projects, including those on plating and related technologies. Investigators of plating with a background in electroanalytical chemistry were rare in earlier days. But, recently, many workers have unequivocally demonstrated the virtue of electroanalytical approaches for elucidating problems in surface finishing, both on the level of fundamental investigations and the control of practical processes.

Electroanalytical chemistry has made great progress since the mid-1950s and its fundamentals are now well explored and understood. Furthermore, recent advances in electronic instrumentation have made electroanalytical devices highly reliable, sensitive, flexible and easy to use. Electroanalytical methodology is now in a mature stage, and its applications to real chemical problems are increasing rapidly. These considerations led me to believe that it would be appropriate to take this opportunity to review how electroanalytical methods have contributed in recent years to our field of interest.

It is my great pleasure to present this lecture in honor of the late Dr. William Blum, the first winner of the AES Scientific Achievement Award, in 1958. He contributed greatly to the advancement of the fundamental and practical aspects of electroplating and allied technologies.

Scope of lecture

Electroanalytical chemistry, as defined by Lingane in 1953,[1] comprises methods of chemical analysis based on electrochemical reactions at metallic electrodes in electrolytes. This definition has since been considerably broadened.[2] Extensive studies of fundamental principles of various electroanalytical techniques carried out over more than 30 years proved that these techniques are highly useful not only for chemical analysis but for investigations of industrially important electrochemical areas such as electroplating, corrosion, batteries and electrosynthesis. Consequently, the term "electroanalytical methods" is now used in a much broader sense and practically synonymously with "electrochemical methods."[3]

This review covers applications of the following methods to problems in plating: DC and AC polarography, differential pulse polarography, square-wave voltammetry, linear sweep and cyclic voltammetry, AC cyclic voltammetry, and impedance measurements. The conventional steady-state polarization measurement has been a standard practice in the investigation of plating systems and is not included in this review. Likewise more conventional and classical electroanalytical methods such as potentiometry and potentiometric titration are excluded. Descriptions of the principles and theories of the various methods are kept to a minimum; emphasis is placed on applications. For detailed accounts of the principles and theories, Refs. 3 and 4 are recommended.

DC polarography

Classical DC polarography with the dropping mercury electrode has been used to analyze and monitor the concentrations of bath constituents and impurities, and to obtain insight on the kinetics and reaction mechanisms involved in plating processes. For example, a polarographic study[5-7] of gold plating processes from acidic and neutral electrolytes containing cyanoaurate, $Au(CN)_2^-$, led to the finding that the trivalent gold complex, $Au(CN)_4^-$, forms at the commonly used platinum or platinized titanium anode and tends to accumulate in the bath to a steady level. It has been shown that the accumulation of this species is at least partly responsible for the reduced current efficiency observed with aged plating baths.

The decreased efficiency results from the greater amount of electricity required to reduce the trivalent species (three faradays per mole) than the monovalent ion (one faraday per mole). Figure 1 compares classical, current-sampled DC polarograms obtained with fresh and used baths diluted with a mixture of KOH and EDTA (added to mask the effect of Co^{+2}, which was present as the hardening agent). The single wave from the fresh bath is due to the reduction of $Au(CN)_2^-$ to gold amalgam:

$$Au(CN)_2^- + Hg + e^- \rightarrow Au(Hg) + 2CN^- \qquad (1)$$

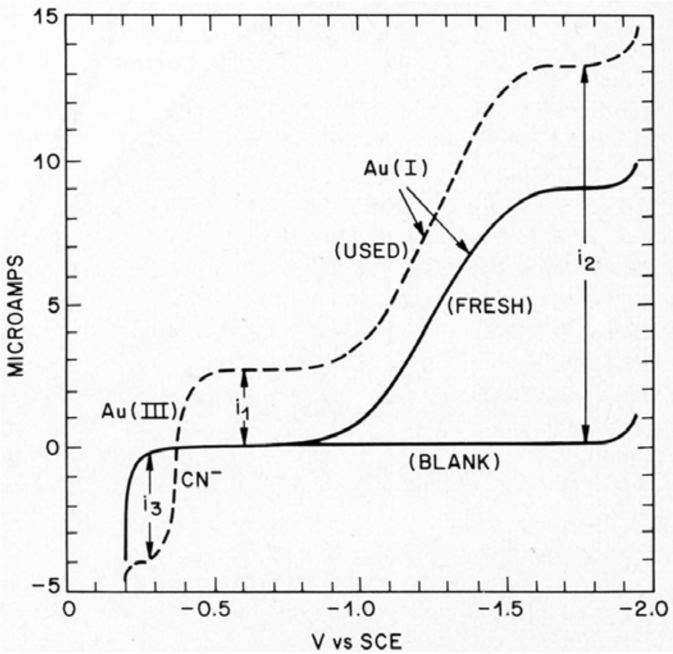


Figure 1 - DC polarograms of fresh and used hard gold plating bath (Sample diluted 20× in 1M KOH containing 0.05M EDTA and 0.005% polyacrylamide.)

The used bath gave two additional waves: a cathodic wave (i_1) preceding the Au(I) wave, and an anodic wave (i_3) preceding this cathodic wave. It has been shown that the extra cathodic wave is due to the reduction of the trivalent gold complex, $Au(CN)_4^-$, to the monovalent species:

$$Au(CN)_4^- + 2e^- \rightarrow Au(CN)_2^- + 2CN^- \qquad (2)$$

whereas the anodic wave results from the oxidation of mercury (the electrode) in the presence of free cyanide:

$$Hg + 2CN^- \rightarrow Hg(CN)_2 + 2e^- \qquad (3)$$

where the free cyanide is produced at the cathode during plating. The half-wave potentials of these two waves are so close to each other that they give the appearance of a composite wave for a reversible redox couple. Measuring diffusion-limiting currents at the three plateau regions (i_1, i_2 and i_3) allows monitoring of concentration changes of the three species, and this principle was utilized in the design of automatic and semi-automatic gold bath analyzers and controllers.[8,9]

In the fundamental investigation of the plating system[6,7] this analytical method was used to study the kinetics of accumulation of Au^{+3} with the use of different anode materials. This study led to the finding that the Au^{+3} accumulation can be minimized by replacing the platinum anode with a low-polarization type such as DSA®, as illustrated in Fig. 2. The figure shows the concomitant stabilization of current efficiency as well. The polarographic method was also utilized to develop a chemical method for reducing the trivalent gold species back to the monovalent state using a suitable reducing agent such as nydrazine.[6]

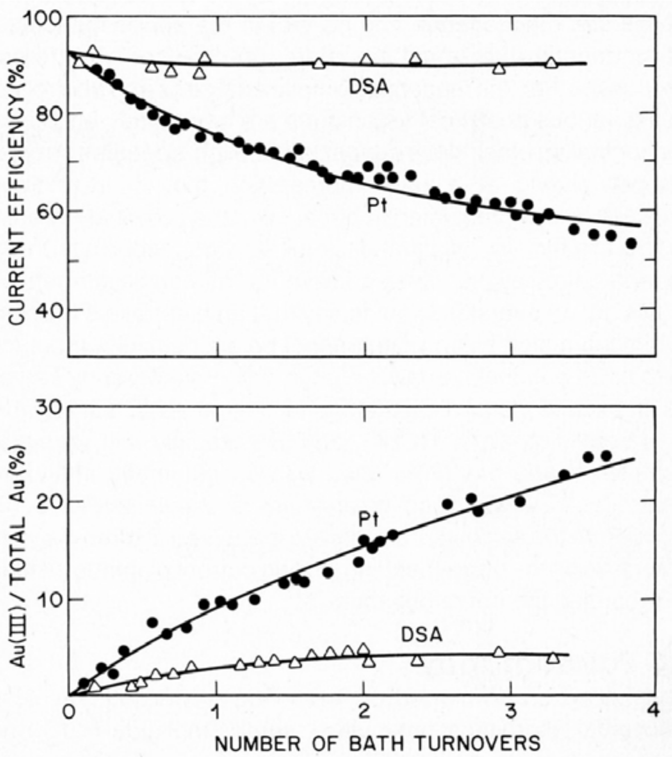


Figure 2 - Effect of anode material on Au^{+3} formation and plating current efficiency (additive-free hard gold bath[5]).

The electroless (autocatalytic) deposition of gold from a solution containing $KAu(CN)_2$, KBH_4, KCN and KOH[10] involves the reduction of $Au(CN)_2^-$ by BH_3OH^-, which is formed as an intermediate in the hydrolysis of BH_4^-:

$$BH_4^- + H_2O \rightarrow BH_3OH_3^- + H_2 \qquad (4)$$

$$BH_3OH^- + 3H_2) \rightarrow B(OH)_4^- + 3H_2 \qquad (5)$$

$$BH_3OH^- + 3Au(CN)_2^- + 3OH^- \rightarrow B(OH)_4^- + (3/2)H_2 + 3Au + 6CN^- \qquad (6)$$

The hydrolysis intermediate adsorbed on the substrate surface serves as the actual reducing agent; it has a much stronger reducing power (oxidized at much more negative potentials) than BH_4^-. Because the rate of electroless gold deposition depends on the concentration of reducing agent, it is important to know how it changes with bath operating time. Polarography was employed to obtain this information.[11]

As shown in Fig. 3, the two borohydride species, BH_3OH^- and BH_4^-, are oxidized at widely separated potentials. Measuring currents at two potentials corresponding to the plateau regions of the two waves as a function of hydrolysis time allows calculation of rate constants for Reactions 4 and 5. These rate constants can then be used to calculate the variation in concentration of the borohydride species with time (Fig. 4).[11] These data are useful in establishing a replenishment schedule during bath operation.[12]

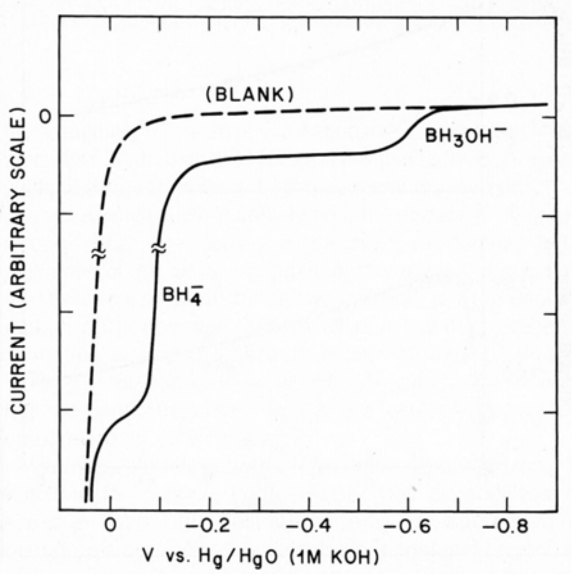


Figure 3 - DC polarogram of a borohydride solution in 0.2M KOH at 75°C.

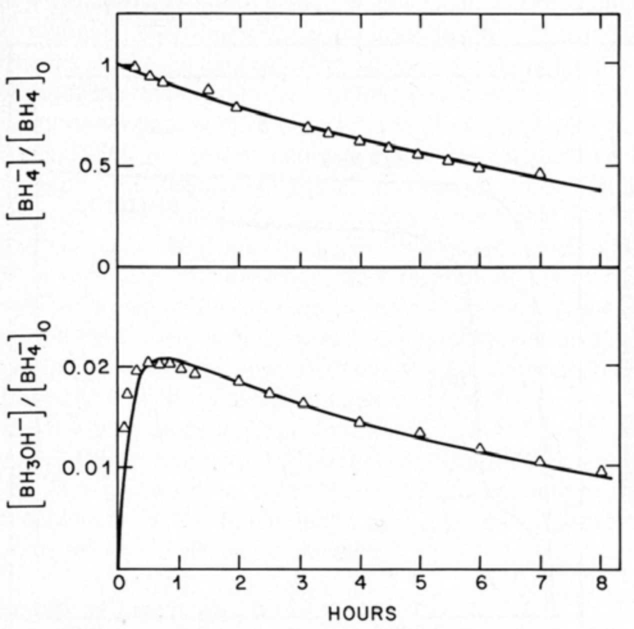


Figure 4 - Variation of concentrations of BH_4^- and BH_3OH^- with time during electroless gold[4] plating in 0.2M KOH at 75°C.

The rate of electroless plating reactions generally is much more concentration-dependent than for electroplating. Therefore, maintenance and control of the concentrations of bath constituents must be more precise for electroless processes. For this reason, automatic analyzers and controllers using various analytical techniques are now widely employed for controlling electroless copper baths. High-speed electroless copper plating at a rate approaching that of electrolytic processes is of great interest because of the potential increase in the productivity of printed circuit boards, especially those manufactured by the "partly additive" or "fully additive" method.

It is not an overstatement to say that an electroless process with such a high plating rate cannot be successful without the help of an automatic analyzer/controller. Polarography serves as an excellent analytical method for this purpose. It is capable of determining Cu^{+2}, HCHO and CN^- rapidly with a single sample[13,14] and has been used with an automatic analyzer / controller.[14] A typical DC polarogram is shown in Fig. 5. To accelerate the analysis, currents are measured at three discrete potentials on the corresponding limiting current plateaus instead of recording the entire polarogram.

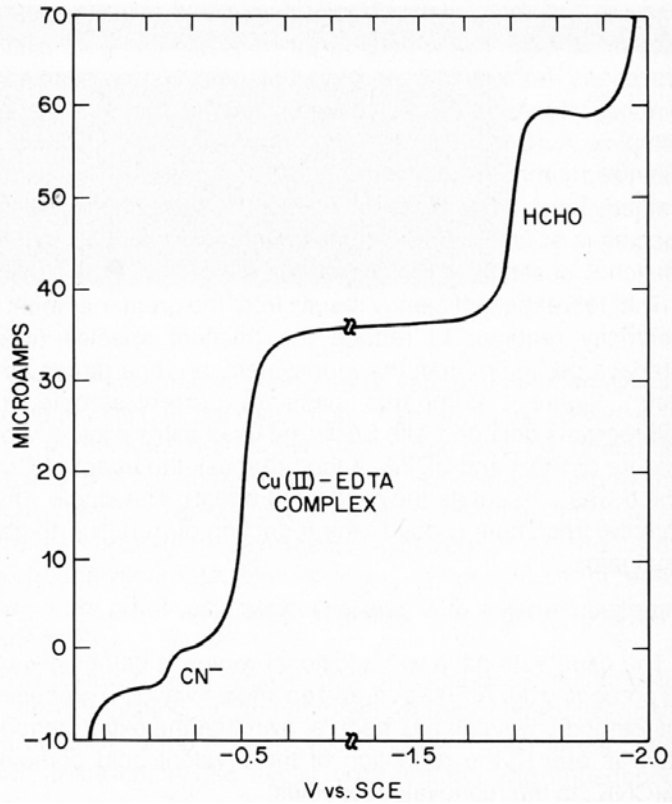


Figure 5 - DC polarogram of an electroless copper bath diluted 10× with 0.1M NaOH.

AC polarography

The polarographic method involving superposition of a sinusoidal alternating potential of small amplitude (<10 mV) onto the scanned DC polarization voltage is called "AC polarography." The measured quantity is the amplitude of the AC current, which is recorded after filtering out the DC component from the total current. The AC current thus measured consists of a faradaic component which results from charge transfer reactions taking place at the electrode and a capacitive component arising from the charging of the electrical double layer at the electrode/solution interface. In the early days of AC polarography, only the total AC current could be measured and the technique suffered from low sensitivity for analytical purposes. This problem was largely eliminated in later years when a phase-sensitive detector was incorporated . It allows separate measurements of the capacitive component, which is 90° out of phase of the applied AC voltage (in the absence of iR drop), and the faradaic component, which is in phase or less than 45° out of phase depending on the nature of the electrode process. Modern AC polarographs are equipped with this capability. To my knowledge, there is no specific report on the application of AC polarography to the analysis or investigation of plating processes. It may be useful, under certain conditions, for the analysis of electro-inactive but surface-active species such as organic additives because of the capability of measuring the capacitive component of the AC current separately from the faradaic component.

Differential pulse polarography

Differential pulse polarography has become extremely popular in recent years for trace analysis because of its high sensitivity. The availability of relatively inexpensive commercial instruments also is an important factor. With this technique, voltage pulses of a small constant height are superimposed on a linear DC ramp. A small pulse is applied near the end of the life of each mercury drop. The current is sampled immediately before application of the pulse and again at the end of the pulse, and the difference between these two currents is recorded as a function of DC potential. The result is a highly effective discrimination against the capacitive current resulting from the charging of the double layer, which makes it possible to obtain enhancement of the detection limit by a factor of at least 100 as compared to DC polarography.

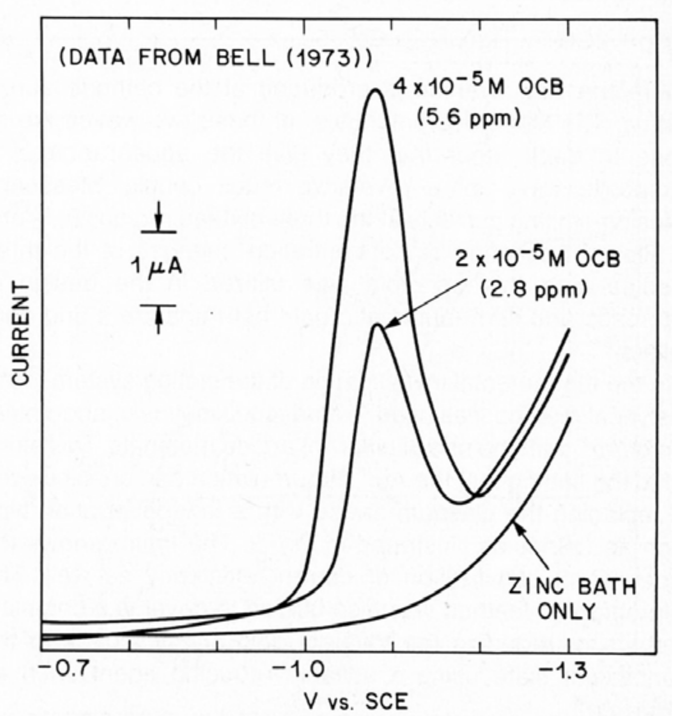
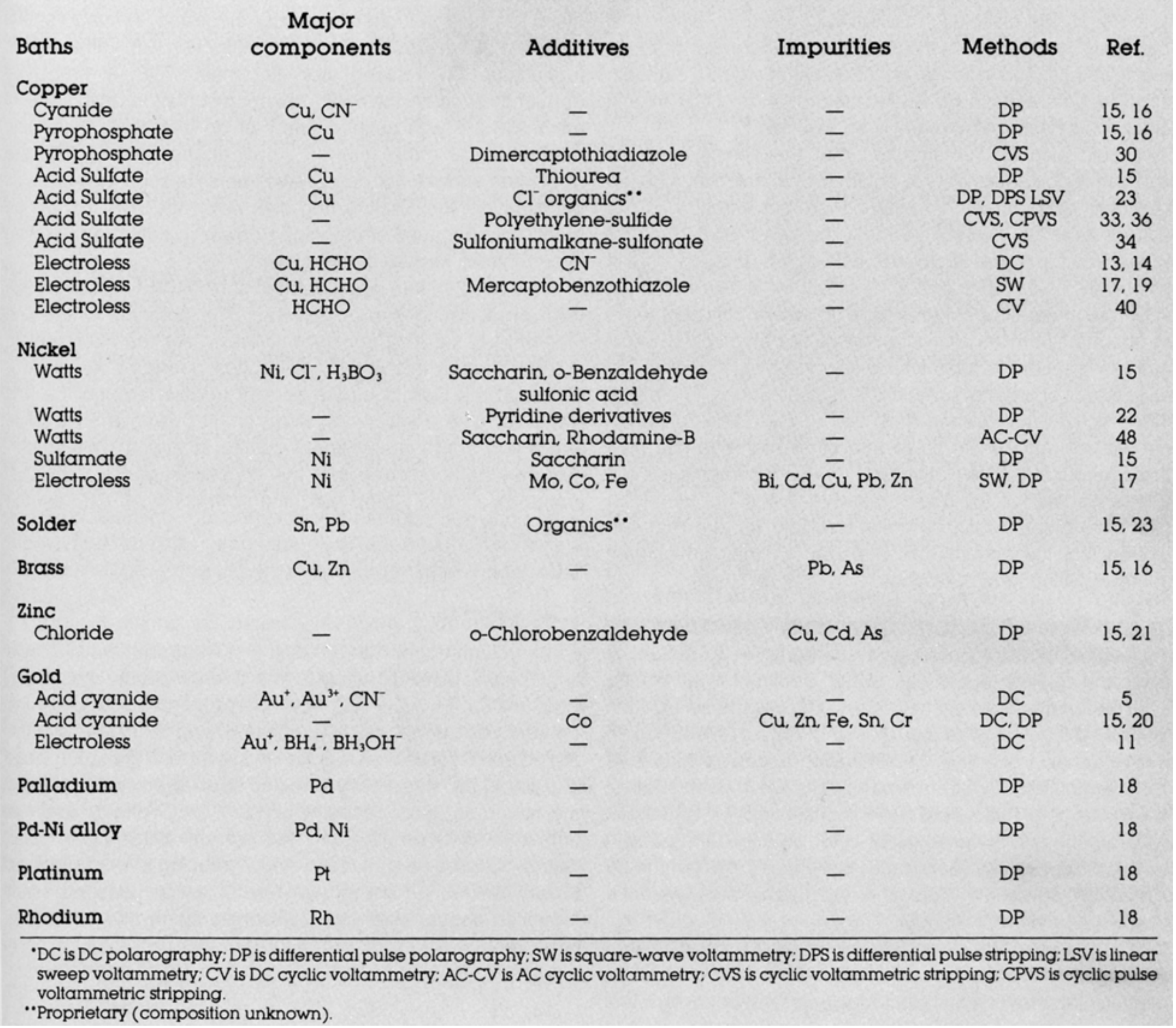


Figure 6 - Differential pulse polarograms of o-chlorobenzaldehyde (OCB) in a chloride zinc plating bath in supporting electrolyte containing 0.6M acetate buffer (pH=5) and 0.04M EDTA (from Ref. 21).

A number of plating baths have been analyzed using this technique for major constituents as well as additives and impurities (Table 1). To illustrate the sensitivity, differential pulse polarograms of o-chlorobenzaldehyde (brightening agent) in a chloride zinc bath are reproduced in Fig. 6.[15,21] It has been shown that this compound can be determined at concentrations as low as 0.1 ppm (7×10^{-7}M).

In spite of the popularity of this method, it should not be considered a universal technique. It can be used only where corresponding DC polarograms give waves with a well-defined sigmoidal current-potential relationship. For example, if the species to be analyzed begins to be reduced at potentials more positive than the dissolution potential of mercury, differential techniques do not produce a defined peak. Differential methods are also inapplicable when an anodic wave overlaps a cathodic wave. The determination of Au^{+3} in the presence of CN^{-} in gold plating baths described already is an example.[18]

Table 1 - Plating baths analyzed by polarography and voltammetry.



Baths	Major components	Additives	Impurities	Methods	Ref.
Copper					
Cyanide	Cu, CN^-	—	—	DP	15, 16
Pyrophosphate	Cu	—	—	DP	15, 16
Pyrophosphate	—	Dimercaptothiadiazole	—	CVS	30
Acid Sulfate	Cu	Thiourea	—	DP	15
Acid Sulfate	Cu	Cl^- organics**	—	DP, DPS LSV	23
Acid Sulfate	—	Polyethylene-sulfide	—	CVS, CPVS	33, 36
Acid Sulfate	—	Sulfoniumalkane-sulfonate	—	CVS	34
Electroless	Cu, HCHO	CN^-	—	DC	13, 14
Electroless	Cu, HCHO	Mercaptobenzothiazole	—	SW	17, 19
Electroless	HCHO	—	—	CV	40
Nickel					
Watts	Ni, Cl^-, H_3BO_3	Saccharin, o-Benzaldehyde sulfonic acid	—	DP	15
Watts	—	Pyridine derivatives	—	DP	22
Watts	—	Saccharin, Rhodamine-B	—	AC-CV	48
Sulfamate	Ni	Saccharin	—	DP	15
Electroless	Ni	Mo, Co, Fe	Bi, Cd, Cu, Pb, Zn	SW, DP	17
Solder	Sn, Pb	Organics**	—	DP	15, 23
Brass	Cu, Zn	—	Pb, As	DP	15, 16
Zinc					
Chloride	—	o-Chlorobenzaldehyde	Cu, Cd, As	DP	15, 21
Gold					
Acid cyanide	Au^+, Au^{3+}, CN^-	—	—	DC	5
Acid cyanide	—	Co	Cu, Zn, Fe, Sn, Cr	DC, DP	15, 20
Electroless	Au^+, BH_4^-, BH_3OH^-	—	—	DC	11
Palladium	Pd	—	—	DP	18
Pd-Ni alloy	Pd, Ni	—	—	DP	18
Platinum	Pt	—	—	DP	18
Rhodium	Rh	—	—	DP	18

*DC is DC polarography; DP is differential pulse polarography; SW is square-wave voltammetry; DPS is differential pulse stripping; LSV is linear sweep voltammetry; CV is DC cyclic voltammetry; AC-CV is AC cyclic voltammetry; CVS is cyclic voltammetric stripping; CPVS is cyclic pulse voltammetric stripping.

**Proprietary (composition unknown).

It should also be remembered that the sensitivity of all methods giving derivative-type polarograms, which include the differential pulse method, depends on the kinetics of the electrode reaction involved. Namely, the sensitivity is high for fast reactions giving reversible DC polarographic waves, but is significantly lower (up to about 10 times) for slower reactions giving quasi-reversible or irreversible DC waves. This contrast is very important from the analytical viewpoint, because the rate of electrode reactions is often affected by the presence of a very small amount of organic surface-active substances. Therefore, surface-active additives and impurities may affect the response obtained with differential pulse and other methods that give current output of the derivative type. These comments are not made to discourage the use of these methods, but merely to make the reader aware of limitations and factors that are important but not generally emphasized by their advocates, particularly in the area of plating.

Square-wave polarography and voltammetry

In the original form of square-wave polarography, developed by Barker and Jenkins as early as 1952,[24] a train of small square waves is superimposed on the linearly changing DC polarization potential, which is applied to a dropping mercury electrode. In order to achieve effective discrimination against the double-layer charging effect, current is sampled twice in each square-wave cycle, once just before the end of a half-cycle and again just before the end of the next half-cycle, and the difference in the two current values (amplitude) is recorded against the DC polarization potential. Thus, this technique also yields a derivative-type current readout.

Although the originators demonstrated its capability of achieving a highly enhanced sensitivity (4×10^{-8}M and 10^{-6}M for reversibly and irreversibly reduced species, respectively), this method suffered a noise problem resulting from variations in response of the capillary used as the electrode. The change in surface area associated with the growth of each mercury drop was also considered undesirable.

A modern version of square-wave polarography employs a static mercury drop electrode, eliminating the difficulties mentioned above. Thus, the technique[**] is now called "square-wave voltammetry." Here, a square wave is superimposed on a potential staircase rather than a continuously changing ramp, and the entire potential scan is completed on a single mercury drop, typically within several seconds. This fast analysis capability, combined with the enhanced sensitivity (three to four times that of differential pulse polarography)[26] is a unique feature of square-wave voltammetry. This operating mode is now available on some commercial polarographs. Professor Robert Osteryoung, an eminent electroanalytical chemist, has been quoted[26] as saying, "From the analytical point of view, square-wave voltammetry is the technique most likely to dominate pulse voltammetry in the future."

Square-wave voltammetry has recently been applied to the analysis of electroless nickel baths for nickel as well as metallic impurities and alloying elements. It has also been employed for the analysis of electroless copper baths for Cu^{+2}, HCHO, and mercaptobenzothiazole (stabilizer),[16] as shown in Table 1.

Linear sweep voltammetry

In linear sweep (or scan) voltammetry, the applied potential is scanned at a constant rate in one direction only using a solid electrode or a stationary mercury electrode. Among various types of solid electrodes used in conjunction with voltammetric techniques, the rotating disk electrode (RDE) is employed frequently because the mass-transport conditions at this type of electrode are well defined and can be described by simple mathematical expressions.[3] Applications of the RDE are numerous and will not be reviewed here as such. However, its modification, the rotating ring-disk electrode (RRDE), will be mentioned because of its unique power in detecting reaction intermediates formed during plating.

In the RRDE a thin ring electrode surrounds a disk electrode with an insulating gap in between. The potential of the ring electrode is set at a constant value, where the intermediate product formed at the disk electrode undergoes an electrochemical reaction to cause current to flow through the ring electrode. One of the early systems studied using an RRDE was deposition from acidic copper sulfate solutions. This study[27] elegantly demonstrated that the deposition of Cu from Cu^{+2} proceeds in two steps with the formation of Cu^+ as the intermediate:

$$Cu^{+2} + e^- \rightarrow Cu^+ \tag{7}$$

$$Cu^+ + e^- \rightarrow Cu \tag{8}$$

The voltammogram at the disk (Pt) electrode shows only a single wave corresponding to the overall copper deposition reaction: $Cu^{+2} + 2e^- \rightarrow Cu$ with no apparent indication of the formation of Cu^+ as an intermediate. Using an RRDE with the ring potential set at a value where the reverse of Reaction 7 can take place, Cu^+ was clearly detected as an anodic current at the ring electrode. More recently, Hayashi and Yokoi[28] used this technique to investigate why the current efficiency in pulse plating of copper decreases with decreasing average current density and with increasing off-time. They demonstrated that deposited copper chemically dissolves during the off-time to form Cu^+:

$$Cu^{+2} + Cu \rightarrow 2Cu^+ \tag{9}$$

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[*] The term "voltammetry" was coined by Kolthoft and Laitinen[25] to describe the measurement of current-voltage characteristics at any microelectrodes, including the dropping mercury electrode. It is now most frequently used to refer to the measurement with electrodes other than the dropping mercury electrode.

It was observed that pulse plating with low duty cycles promotes layer growth and yields deposits with considerably smoother surfaces than those obtained by either DC or pulse plating with high duty cycles. This effect was attributed to Reaction 9, which preferentially dissolves protrusions such as pyramidal growths on the surface during the off-time.

Another interesting application of the RRDE is concerned with the question of whether Cu^+ is formed during electroless copper plating. The inclusion of Cu_2O has been suggested as a cause of poor ductility of electroless copper. A study I carried out using an RRDE showed that Cu^+ indeed forms during the reduction of Cu^{+2} from alkaline media with or without tartrate, but not from solutions containing EDTA as the complexing agent (Fig. 7). In these experiments the disk (Pt) potential was scanned in the negative direction at a speed of 17 mV/sec, while the ring (Au) electrode was held at 0 V_{SCE}.

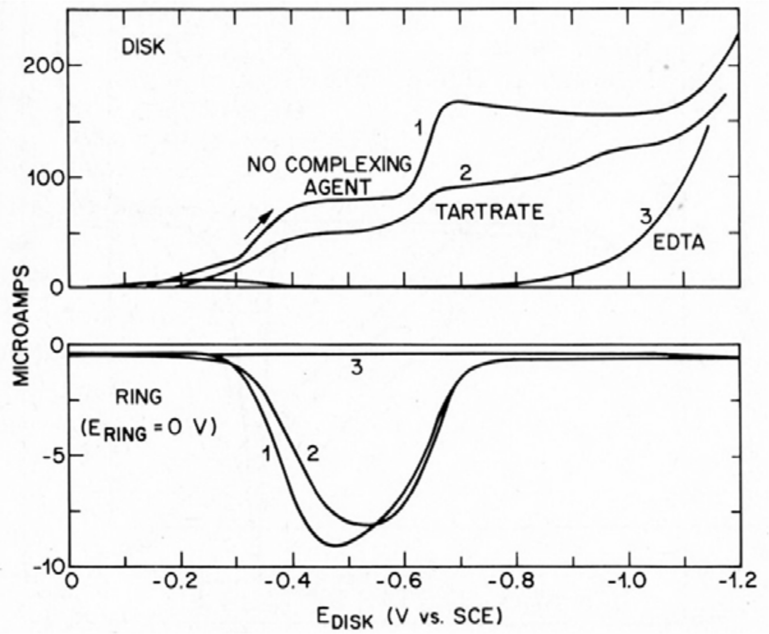


Figure 7 - Linear sweep voltammograms at a rotating ring-disk electrode for the reduction of Cu^{+2} (4×10^{-4}M) in 0.5M NaOH containing different complexing agents.

The term "linear sweep voltammetry" often refers to techniques using much faster scan rates than that indicated above (*e.g.*, 50 to 200 mV/sec or faster). Linear sweep "stripping" voltammetry using a hanging mercury drop electrode was recently developed to analyze an acid copper sulfate bath for organic additives.[23] With this technique the potential is scanned rapidly in the anodic direction from a suitable initial potential where copper deposition takes place. During the anodic sweep the deposited copper is stripped off, giving rise to a peak in the current-potential curve. The height of the stripping peak decreases with increasing additive concentration because of the inhibition effect of the additive on the copper deposition process. This inhibition effect forms the basis for this analytical method.

DC cyclic voltammetry

When the direction of potential sweep is reversed at a preset value and the current recording continued back to the initial starting potential, the technique is called "cyclic voltammetry." This is perhaps the most widely used electroanalytical method for studying electrode processes. The technique allows both the reduction and oxidation processes to be studied quickly from one experiment. The general theory of this method is well developed.[3] Applications for plating are numerous and include studies of reaction mechanisms, optimization of plating conditions, and analysis and control of solutions. Only a few examples will be reviewed here to illustrate the usefulness of the method.

Palladium plating has recently received much attention for electrical contact applications as a substitute for gold. Early palladium processes suffered from the formation of microcracks resulting from the codeposition of hydrogen, leading to the formation of β-

PdH_x phase. This phase spontaneously transforms into α-PdH_x with considerable lattice contractions, causing stress in the deposit. Therefore, it is necessary to minimize the codeposition of hydrogen.

The results of the cyclic voltammetric study recently reported by Abys[29] demonstrate very clearly the usefulness of this technique for finding conditions where the separation of palladium and hydrogen deposition is at maximum. As illustrated in Fig. 8 (solid line), two current peaks are obtained during the cathodic scan at pH 11.5 and 23°C in the system studied. A stationary electrode was used. The first peak is due to the deposition of palladium metal from the palladium complex and the second is attributed to the formation of palladium hydride. The final current rise is due to the evolution of hydrogen. The reverse scan yields an anodic peak that results from the oxidation of the hydride, which has just been formed during the cathodic scan. In the dashed curve obtained at pH 12.5 and 80°C, the cathodic hydride peak is absent, and the potential for palladium deposition is greatly shifted in the positive direction, yielding a wide separation from the hydrogen evolution potential. Conditions for minimizing the hydride formation were established by studying systematically the effects of various variables on the anodic hydride peak. Cyclic voltammetry was used very effectively in this example for optimizing plating conditions.

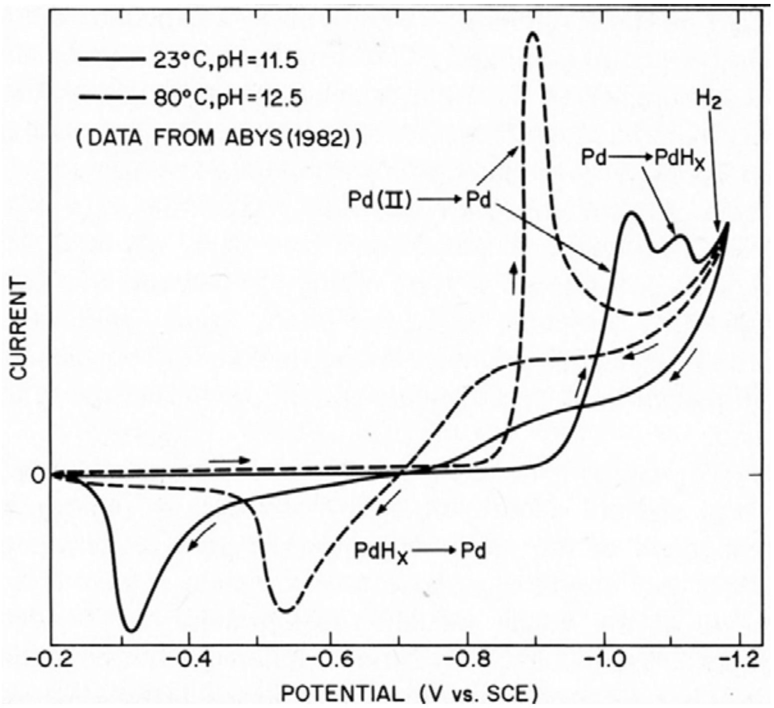


Figure 8 - DC cyclic voltammograms of a palladium plating solution at a stationary platinum electrode (from Ref. 29).

Another noteworthy application of cyclic voltammetry was developed by Tench and Ogden[30-35] for the determination of additives in copper plating baths. The maintenance of additive concentrations in the low-ppm range is critical to obtain deposits acceptable for printed circuit boards. The method is based on the fact that the rate of copper deposition at a given potential is a function of additive concentration. (Note that this dependence is also the basis for linear sweep stripping voltammetry, described in the preceding section.) To determine the brightener (dimercaptothiadiazole) concentration in copper pyrophosphate baths, for example, the potential of a rotating platinum disk electrode is cycled at a constant speed between two preset values, so that a small amount of copper is alternately deposited on the platinum electrode and stripped off by anodic dissolution. Thus, the technique is called "cyclic voltammetric stripping" (CVS).[30] In Fig. 9,[32] copper deposition occurs between -0.3 and -0.7 V for both sweep directions, and the deposited copper is stripped off on the anodic sweep between -0.3 and -0.5 V. The area under the stripping peak corresponds to the amount of copper deposited for that cycle. The peak areas for the two voltammograms show that the copper deposition rate is strongly dependent on the additive concentration. This is the basis for the measurement of the effective concentration of the additive.

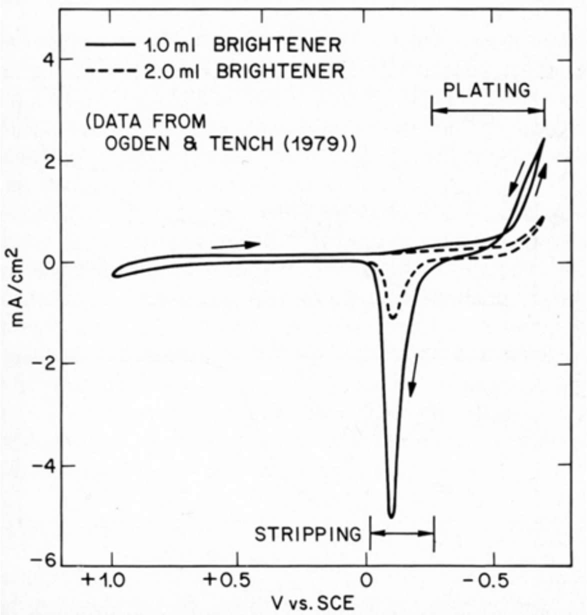


Figure 9 - Cyclic stripping voltammograms of a pyrophosphate copper plating bath containing different amounts of brightener (from Ref. 32).

The technique was used not only for maintenance and control of the plating bath but to gain insight on the function of additives. Tench and Ogden[31] found that copper deposition is decelerated with increasing brightener concentration in the higher concentration range, whereas in the lower concentration range the copper deposition is accelerated. In other words, there is a maximum in the plot of plating rate against brightener concentration. This fact, in combination with mass-transport considerations, explains why leveling results when the brightener concentration is sufficiently high. More significantly, it explains why the malfunctioning called "foldback" occurs during through-hole plating of multilayer circuit boards when the brightener concentration is too low or the solution agitation is insufficient.

The CVS technique was subsequently extended to the analysis of additives in acid copper sulfate baths.[33-36] Both polyether-sulfide-based additives[33] and sulfoniumalkanesulfonate-based additives[34] were analyzed. It was also shown that chloride, another additive generally used with acid copper sulfate baths, can be analyzed simply by extending the anodic potential sweep to the region where a limiting current is obtained for the oxidation of Cl^-. It has been amply demonstrated that the method is useful not only for analytical purposes but for obtaining information on the kinetic effects of plating variables such as agitation, temperature and concentration.

It should be noted that the additives studied by Tench and coworkers were all proprietary, and exact compositions were not known. Nevertheless, their analysis of CVS data demonstrates that even without knowledge of chemical compositions, it is possible to obtain valuable insight on the effects of various components of additives (*e.g.*, wetting and brightening/leveling agents). Furthermore, it has been demonstrated that the CVS technique allows separate determination of such individual additive components.[35] The underlying principle is based on the fact that the wetting agent and the brightener exert opposing effects on the copper deposition kinetics, and these effects appear in separate ranges of the concentration of the proprietary additive containing both components.

Bath contaminants, which alter the conditions of the electrode surface, complicate the application of the CVS technique, but it has been shown recently[36] that this problem can be greatly mitigated by employing a modified CVS method called "Cyclic Pulse Voltammetric Stripping" (CPVS), in which the electrode potential is changed by sequentially stepping between plating, stripping, cleaning and equilibrating potentials in order to maintain the electrode in a clean and reproducible state.

It is of interest to note that, at least in one instance, a cyclic potential sweep was used as an actual plating technique.[37] A crack-free film of ruthenium (5-6 µm thick) was plated from an $(NH_4)_3(Ru_2NCl_8(H_2O)_2)$ bath. In usual DC plating, it is not possible to obtain crack-free ruthenium deposits with a thickness greater than about 2 μm because of the codeposition of impurities such as lower ruthenium oxides and hydrogen. In the potential sweep mode, the potential is cycled repeatedly between +0.15 and -0.60 V versus an Ag/AgCI reference electrode at a rate of 50 mV/sec. The impurities codeposited with ruthenium during the cathodic cycle are removed by oxidation during the anodic cycle. That this is indeed what happens during the course of potential cycles has been shown by a cyclic voltammogram recorded during the plating.

Cyclic voltammetry has recently been used extensively in several studies related to electroless copper plating: an investigation of the effect of various organic additives on cathodic and anodic partial reactions,[38] a study of the effect of cyanide on the anodic oxidation of formaldehyde,[39] and an attempt to use a cyclic voltammetric technique for monitoring formaldehyde concentration.[40] Cyclic voltammetry was employed in a fundamental study of the activity and chemical states of $SnCl_2/PdCl_2$ catalysts used to activate non-conducting surfaces for electroless plating.[41] This study showed that the technique is capable of detecting differences in catalytic activity of the catalysts of the same nominal composition. A cyclic voltammetric technique is also described for *in-situ* analysis of tin and palladium in the mixed catalyst.[42]

AC cyclic voltammetry

The basic principle of AC polarography has been extended to stationary electrodes, including hanging mercury drops, mercury pool and solid electrodes.[43-45] When the DC polarization voltage is cycled between two preset values, the technique is called "AC cyclic voltammetry" (AC-CV). It was first described by Juliard in 1959.[43] The general theory for AC-CV was developed more recently by Bond and co-workers[46,47]

As in AC polarography, an important advantage of AC-CV vs. the DC mode is that with phase-sensitive detection, the former allows separate recordings of faradaic and capacitive components of the AC current and hence yields a considerably less distorted readout. AC-CV retains the quick diagnostic utility of conventional DC cyclic voltammetry, and gives an improved response function that permits quantitative evaluations as precise as those obtained with the conventional, more time-consuming AC impedance measurements.[3]

More recently, Farmer and Johnson[48] described an AC-CV technique with the capabilities of recording faradaic and capacitive currents simultaneously and also of varying the frequency of applied AC voltage. The resulting AC voltammograms were analyzed to calculate charge transfer resistance (a measure of the rate of electrode reaction) and double-layer capacitance as a function of DC polarization potential. This technique was used to study the effects of rhodamine-B (brightener) and saccharin (stress reducer) on the plating of nickel from a Watts bath.

It was shown that detailed examination of the results yields considerable insight on the mechanism of the effects of these additives. For example, it was observed that both additives increase the charge transfer resistance during nickel deposition, but the degree of this effect is much greater for rhodamine-B than for saccharin. It was also observed that the double-layer capacitance is suppressed to a much greater extent with rhodamine-B than with saccharin, the suppression being due to adsorption. Because of the weakness of adsorption, saccharin molecules appear to be partially displaced by adsorbed Ni^{+2} ions during the deposition of nickel. No evidence for such a displacement was observed with rhodamine-B. As far as the measurement accuracy is concerned, much greater accuracy is obtained for double-layer capacitance (±2%) than for charge transfer resistance (±20%).

Because of the high accuracy and also the high sensitivity obtained with this technique for the capacitance measurement, it was proposed to develop a capacitance probe for monitoring additive levels in plating baths. It should be realized, however, that double-layer capacitance is sensitive to the presence of any organic and inorganic surface-active substances in the solution as well as to variations in electrolyte concentrations. Thus, a major challenge facing such an attempt would be to find a way of differentiating between the effects of additives to be monitored and those resulting from changes occurring in the plating solution with time (*e.g.*, the accumulation of extrinsic contaminants and decomposition products of the additives).

AC impedance measurements

With the AC-CV technique described above, charge transfer resistance and double-layer capacitance are calculated from the magnitude of AC currents measured at different phase angles during scanning of DC polarization potential. The two quantities can also be determined at discrete DC potentials using one of many available methods for impedance measurements - for example, a method using an impedance bridge or a more direct method involving measurements of the ratio of stationary amplitudes of AC voltage and current and the phase angle between them.

These discrete techniques are rather time-consuming but have been used in many fundamental studies of plating reactions. Examples include studies on the nucleation and growth of silver deposition,[49] anion effects on nickel electrodeposition,[50,51] effects of adsorbed hydrogen and organic additives (2-butyne-1,4-diol and sodium benzenesulfonate) also in nickel deposition,[52] and effects of N,N-dimethylaniline, thiourea and 2-mercaptobenzothiazole on copper plating from acid sulfate solutions.[53] Electroless nickel plating has also been studied to a limited extent using an impedance method.[54]

A more practical application of AC impedance measurement was described recently by Ohno and co-workers,[55,56] who devised a method for monitoring the instantaneous rate of electroless plating of copper, nickel and cobalt. The basic principle is simple as described briefly below. It is now well established that electroless plating is a "mixed potential reaction," in which the overall reaction consists of partial cathodic and partial anodic reactions proceeding at an equal rate on the surface of the depositing metal. Under steady-state conditions with the reactions controlled by charge transfer processes, the rate of the two partial reactions (= i_{pl} = plating rate) is inversely proportional to the charge transfer resistance, R_t:

$$i_{pl} = \frac{K}{R_t} \qquad (10)$$

where $K = RT/\alpha nF$, in which the symbols have the conventional significance. The total complex impedance involves solution resistance, R_s, double-layer capacitance, C_{dl}, and R_t, and is given by:

$$Z = R_s + \frac{R_t}{1 + j\omega C_{dl} R_t} \qquad (11)$$

where $j = \sqrt{-1}$ and $\omega = 2\pi f$ (f is frequency), and the second term on the right-hand side is the impedance resulting from the charge transfer reaction and the double layer. It can be understood easily from this equation that R_t, and hence the plating rate, can be found from impedance values at two extreme frequencies: $Z(\omega \rightarrow 0) \rightarrow R_s + R_t$ ($+R_o$) and $Z(\omega \rightarrow \infty) \rightarrow R_s$ ($=R_\infty$); hence Rt $= Z(\omega \rightarrow 0) - Z(\omega \rightarrow \infty) = R_o - R_\infty$. When one of the partial reactions is under diffusion control, the expression becomes more complex, but it has been shown that the charge transfer resistance in this case can also be determined from impedance values measured at only two frequencies. The relationship of Eq. 10 has been verified experimentally for electroless copper (Fig. 10[56]) in which the plating rate was determined gravimetrically. Similar verifications have been reported for electroless plating of nickel and cobalt.[56] A simple automatic rate monitor has been constructed based on this principle.

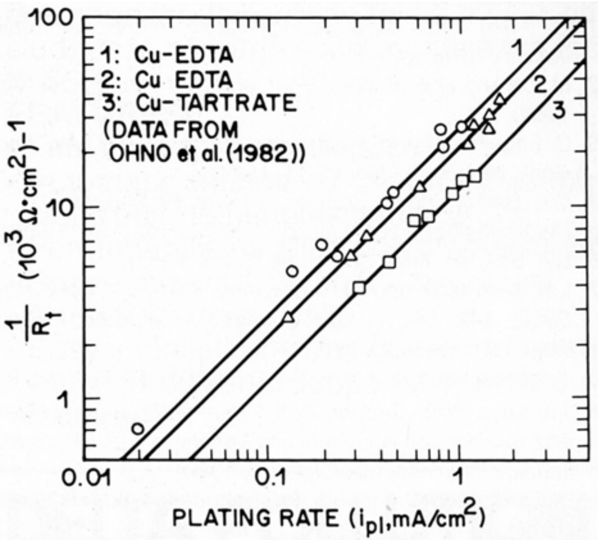
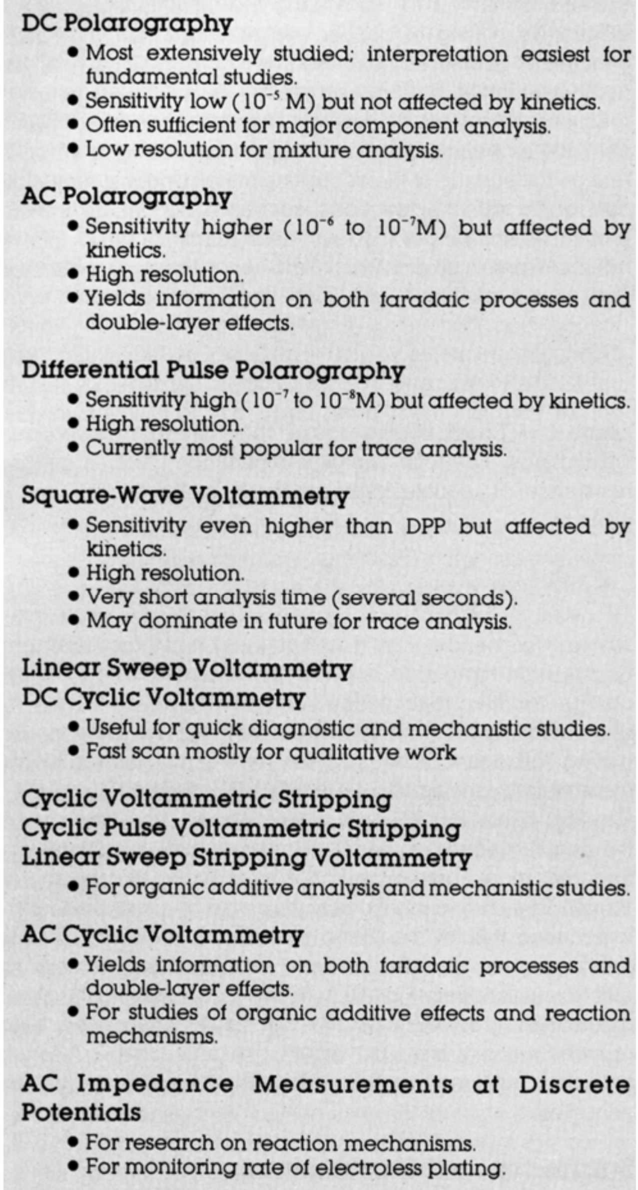


Figure 10 - Relationship between reciprocal charge transfer resistance of electroless copper plating baths determined from impedance measurements and gravimetrically determined plating rate (from Ref. 56).

Summary and conclusions

A review of recent applications of various electroanalytical techniques to the field of finishing has been presented here. Advantages, disadvantages and limitations have been stated for each method. They are briefly summarized in Table 2 for ready comparison. The fundamentals of all methods are now sufficiently well understood, and the instrumentation has advanced to the stage that many of the methods can be performed routinely on commercial instruments.

Table 2 - Comparison of various electroanalytical methods.



DC Polarography

- Most extensively studied; interpretation easiest for fundamental studies.
- Sensitivity low (10^{-5} M) but not affected by kinetics.
- Often sufficient for major component analysis.
- Low resolution for mixture analysis.

AC Polarography

- Sensitivity higher (10^{-6} to 10^{-7}M) but affected by kinetics.
- High resolution.
- Yields information on both faradaic processes and double-layer effects.

Differential Pulse Polarography

- Sensitivity high (10^{-7} to 10^{-8}M) but affected by kinetics.
- High resolution.
- Currently most popular for trace analysis.

Square-Wave Voltammetry

- Sensitivity even higher than DPP but affected by kinetics.
- High resolution.
- Very short analysis time (several seconds).
- May dominate in future for trace analysis.

Linear Sweep Voltammetry
DC Cyclic Voltammetry

- Useful for quick diagnostic and mechanistic studies.
- Fast scan mostly for qualitative work

Cyclic Voltammetric Stripping
Cyclic Pulse Voltammetric Stripping
Linear Sweep Stripping Voltammetry

- For organic additive analysis and mechanistic studies.

AC Cyclic Voltammetry

- Yields information on both faradaic processes and double-layer effects.
- For studies of organic additive effects and reaction mechanisms.

AC Impedance Measurements at Discrete Potentials

- For research on reaction mechanisms.
- For monitoring rate of electroless plating.

Experiences have shown that electroanalytical approaches are useful not only for solving practical chemical problems such as the analysis and control of electrolytic and electroless plating processes, but for obtaining an improved understanding of the effects of variables, including those of additives. It is recognized that mechanisms by which various additives function in plating processes are still poorly understood. One reason the progress in this area has been slow is the difficulty in performing quantitative analysis of such additives, often a mixture of two or more compounds, in ppm and ppb ranges in the presence of high concentrations of electrolytes. It is gratifying to see that electroanalytical methods have begun to make some substantial contributions in this respect.

Precise control of finishing processes is becoming increasingly important as the demand for products becomes more stringent with respect to functional properties. This is especially true for applications in high-technology areas. Good process control requires effective analytical techniques and sensors for monitoring purposes. It should be emphasized that good process control also requires a scientific understanding of the effects of all variables, including those of additives and impurities. This can be achieved only through systematic research efforts, and good analytical techniques are needed for this purpose. It is hoped that this lecture will stimulate further applications of the powerful electroanalytical methods for improved control and a better understanding of existing and emerging finishing processes.

Acknowledgments

Thanks are due all of my former colleagues at AT&T Bell Laboratories for their collaboration for many years until my recent transfer to Bell Communications Research. Special thanks to Dr. Dennis R. Turner for his continued encouragement, understanding and advice since I first joined his group in 1963. I also thank Catherine Wolowodiuk and Douglas W. Graham for assisting and collaborating with me in much of my experimental work, including that reviewed in this lecture.

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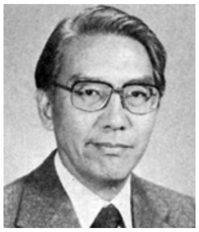
About the author

This piece was written at the time Dr. Okinaka was announced as the recipient of the 1984 Scientific Achievement Award.



Dr. Yutaka Okinaka was named the 1984 recipient of the AESF Scientific Achievement Award on July 19 during AES SUR/ FIN 1984, New York. The announcement was made by James E. Voytko, CEF, chairman of the Scientific Achievement Award Committee. The award is presented annually to recognize an individual who has made outstanding scientific contributions advancing the theory and practice of electroplating and allied sciences, raised the quality of products or processes, or enhanced the dignity of the profession.

Today, Dr. Okinaka conducts research on plating and other finishing operations at Bell Communications Research, Inc., which was formed as a result of the AT&T divestiture in 1984. He joined Bell Laboratories as a member of the technical staff in 1963. His initial work there centered on rechargeable batteries. Dr. Okinaka came to the U.S. in 1954 from his native Japan to work as a research fellow and instructor at the University of Minnesota, where he remained until 1960. From 1960-63, he was an assistant professor of electrochemistry at Tohoku University.

Dr. Okinaka has published about 60 papers in the technical literature, including 25 on plating, and holds 11 patents on subjects relating to surface finishing. He received his B.S. and Ph.D. degrees from Tohoku University, Sendai, Japan, in 1948 and 1959, respectively. The award winner’s contributions have been primarily in electroless gold plating, electrolytic gold plating and electroless copper plating.

Dr. Okinaka's invention in 1969 of an electroless process using borohydride or amineborane was the first truly autocatalytic gold process. Other electroless gold processes known at the time were based on either a displacement reaction with the substrate or its catalytic activity. When a piece of gold was placed in such baths, no plating took place, and therefore the maximum gold thickness achievable was very limited. Dr. Okinaka's bath obviated this problem. Since the initial publication in 1970, he and his coworkers at Bell Laboratories have published papers on complete characterization of the plating process, a fundamental study of the reaction mechanism, the evaluation of deposit properties, and applications for the fabrication of integrated circuits and 11 I-V semi-conductor devices. The original process is still used routinely, although modified ones have been developed in recent years.

Dr. Okinaka's study in 1978, conducted with Dr. F.B. Koch and others, on the inclusions in cobalt-hardened gold showed that the residue and filtration obtained upon dissolution of the gold deposit in aqua regia is a compound of divalent cobalt and trivalent hexacyano-cobaltate and not an organic polymer as previously thought. This study also demonstrated that both carbon and cobalt are present in the deposit in at least two different forms: carbon as a Co-cyanide complex and an organic compound, and cobalt as an Au-Co alloy and the Co-cyanide complex. In addition, with Dr. S. Nakahara, he studied the microstructure of various types of hard gold deposits and made direct observation of inclusions using transmission electron microscopy. These investigations considerably advanced the understanding of the relationship between the structure and properties of gold deposits.

In 1979, Dr. Okinaka and coworkers developed improved analytical methods for gold and cobalt in gold plating baths. These methods were subsequently used in the automatic gold bath analyzer that they designed and constructed. Unlike the conventional atomic absorption technique, the polarographic method developed by Dr. Okinaka is capable of measuring Au^+ and Au^{+3} separately. This capability led to the discovery that aged gold plating baths contained large amounts of Au^{+3} although the fresh bath is prepared with only Au^+. This finding explained why the current efficiency for gold plating declines with bath age and showed the importance of monitoring Au^{+3} buildup for obtaining good thickness control. Trivalent cobalt is present in aged baths but is inactive as the hardening agent. Therefore, the colorimetric method that Dr. Okinaka developed for cobalt analysis is also more advantageous than atomic absorption spectroscopy because it measures only Co^{+2} instead of the sum of Co^{+2} and Co^{+3}. He won the AES Silver Medal Award in 1980 for a paper reporting the improved methods.

Subsequently, Dr. Okinaka extended this work to develop gold plating systems in which Au^{+3} formation is minimized and plating current efficiency is stabilized. He replaced the conventional Pt-based anode with the dimensionally stable anode (DSA). The low oxygen overpotential of this anode has been shown to be responsible for this success. In recent work with Dr. C.G. Smith, he developed more practical, improved anode compositions that are considerably more stable in the long run than the ordinary Ru-based DSA under the conditions of gold plating.

Dr. Okinaka played a leading role in the development and evaluation of an additive-free hard gold plating process. He showed that hard gold that is essentially free of the abnormally high contact resistance occasionally observed with thermally aged cobalt-hardened gold can be plated from an additive-free bath. The phosphate-based, additive-free system is now being used successfully on a large scale in the U.S. and Japan for high-speed strip plating of contacts and connector terminals. Dr. Okinaka received the AES Silver Medal Award in 1981 for a paper on this study. Also, the Metal Finishing Society of Japan honored him with the Best Paper Award for his presentation on this subject at the 10th World Congress on Metal Finishing in 1980.

His work on electroless copper plating included a study of the reaction mechanism, the development of an automatic analyzer and controller, and an investigation into the cause of deposit brittleness. His work with Dr. S. Nakahara using transmission electron microscopy showed for the first time the inclusion of numerous gas bubbles and voids and produced the first paper describing hydrogen embrittlement of copper.

Dr. Okinaka was honored with the 1981 Research Award of the Electrodeposition Division of the Electrochemical Society for his contributions to gold plating research. In 1982, Bell Labs, honored him with the Distinguished Technical Staff Award for his sustained and significant individual contributions.

Yutaka Okinaka is currently a member of the AES Research Board and supervisor for AES Project 62. He is a divisional editor of the *Journal of the Electrochemical Society* and chairman of the U.S. office of the Electrochemical Society of Japan.