

Investigation of Quantitative and More Practical Analysis Methods Based on the Electrochemical Reactions

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This paper describes the three electrochemical analyses that we have developed. First, voltammetry using strongly alkaline electrolyte (6 M KOH + 1 M LiOH) is explained, in which the reduction peaks of copper oxides (Cu₂O and CuO) and sulfides (Cu₂S etc.) appeared separately. This method enables the selective determination of Cu₂O, CuO and Cu₂S in the form of nm- μ m of layers on copper surfaces which is not always successful with conventional electrolytes such as 0.1 M KCl. Secondly, anodic polarization method is discussed. This is a method for quantitative estimation of pinhole defects on a plated layer of flexible flat cables (FFCs). Optimization of the electrolytes improves the pinhole defect ratios on a gold-plated layer using 5 M H₂SO₄ and on a nickel-plated layer using 7 M KOH to as low as 0.05% and 0.01%, respectively. Finally, bromine addition method is addressed to quantify 10-100 g m⁻³ of 2-butyne-1, 4-diol (BD) in nickel-plating solution. In this method, bromine is electrolytically generated before each analysis is conducted, thereby achieving BD determination with 5 % accuracy.

Keywords: electrochemical analysis, voltammetry, anodic polarization, addition of electrolytically generated bromine

1. Introduction

Electrochemical techniques have been frequently used in the field of chemical analyses including pretreatment, qualitative estimation and quantification. Principal physical quantities obtained by electrochemical measurements are potential (or voltage), current and resistance. Each quantity provides the indication of a driving force, a rate and a barrier against electrochemical reactions. Figure 1 shows a schematic representation of a basic electrochemical reaction. As seen in this figure, oxidant (O_x) transferred from a distantly-positioned electrolyte reacts with electron on the electrode, and then converts to reductant (R_{ed}). In electrochemical analyses, measurements are carried out focusing especially on the interface between a solution and the electrode.



In wide-ranging electroanalytical modes, cyclic voltammetry (CV) is known as one of the most typical method^{(1),(2)} which measures the current sweeping the potential of a working electrode.

It must be noted that a favorable quantitative performance can be often achieved by using an electrochemical method. In particular, coulometry is known as a high-precision method⁽³⁾. Gallium in GaAs was determined with the precision of four significant figures⁽⁴⁾.

Electrochemical analyses have much potential for the study of industrial solution systems including plating, battery and corrosion. For example, cyclic stripping voltammetry (CSV)⁽⁵⁾ has been applied as a standard method for the indirect estimation of brightening agents in copper-plating solution. In this method, oxidation current of copper pre-plated on a platinum electrode is detected in the

course of the anodic polarization. By the suitable control of plating conditions, this method is applicable to the microscale analysis of metal ions in solution samples⁽⁶⁾. In addition, electrochemical impedance spectroscopy (EIS)⁽⁷⁾ has been frequently applied for the study of battery systems, because the performance of battery correlates closely with resistance. In the theory of EIS, two processes (see Fig. 1), that is, mass transfer and charge transfer can be analyzed separately. EIS has also been utilized in the field of corrosion. As the dissolution rate of some metals are inversely related to the polarization resistance⁽⁸⁾ (Stern-Geary formula), the rate can be estimated quantitatively using the resistance obtained by EIS⁽⁹⁾.

Although applicable chemical species are restricted, the method utilizing electrolytic cathodic reduction has been used for estimates of mass of corrosion products. The technique is based on the cathodic reduction of corrosion products on the surface of some metals in an electrochemical cell by using a suitable electrolyte. If each reductive potential of some corrosion products is separate enough, a qualitative and quantitative analysis may be anticipated.

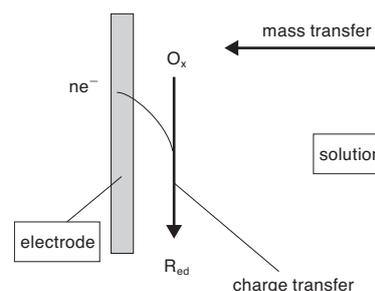


Fig. 1. Schematic representation of basic electrochemical reaction

Analysis equipments for an electrochemical measurement is relatively low-priced and available as a ready-made one. However, standard methods prescribed by such as JIS are relatively sparse. Pourbaix-diagram⁽¹⁰⁾ is helpful to estimate measured data of potentials. However, much of the experience is needed for interpreting the data in light of the diagram, since standard potentials contain no kinetic information. The great discrepancies between a standard potential and measured one are often encountered.

Various electrochemical analyses have been developed in our laboratory. It is part of the reason that existing methods were insufficient for the elucidation of true nature of our problems. In recent years, instrumental analytical techniques have been developed remarkably, however, I realize that electrochemical analyses remain high superiority for specific fields.

In this paper, recently developed three electrochemical analyses are described.

2. Developed Electrochemical Analyses

2-1 Voltammetry using strongly alkaline electrolyte

Because of the high electrical and thermal conductivities, copper and copper alloys are widely used in industrial fields for making electric wires, electronic components, wiring materials and many other products. Although copper is a relatively corrosion-resistant material, various corrosion products can be formed on copper surfaces⁽¹¹⁾ when exposed to the atmosphere containing moisture and pollutants. Troubles such as tarnishing, soldering defect and insufficient insulation may occur according to the amount of corrosion products (e.g., copper oxides and sulfides).

Selective determination of corrosion products is important because each product has different properties for a copper corrosion. Spectrophotometric techniques such as X-ray photoelectron spectroscopy and X-ray diffraction are very useful for qualitative analyses, but not necessarily adequate for quantitative one. The methods based on the electrochemical analysis developed more than 70 years ago⁽¹²⁾ have been applied for selective determination of copper oxides (i.e. Cu₂O and CuO) and a copper sulfide (i.e., Cu₂S) in Japan and overseas.

However, I realized that the selective determination of Cu₂O and CuO was difficult with a conventional method⁽¹³⁾ in practice. Therefore, a new analytical method was explored specially focusing on the separation of Cu₂O and CuO. As a result, it was found that voltammetry using strongly alkaline electrolyte (6 M (= mol dm⁻³) KOH + 1 M LiOH) allowed perfect resolution of Cu₂O and CuO⁽¹⁴⁾. Since then, fundamental researches including quantification of Cu₂O and CuO⁽¹⁵⁾, the analysis of copper sulfides⁽¹⁶⁾, the analytical method for powdered samples⁽¹⁷⁾, the study of the reduction order of copper oxides⁽¹⁸⁾ and the study of reduction mechanism of copper oxides^{(19),(20)} have been developed. Above findings led to the publication of the technical description⁽²¹⁾.

Figure 2 shows the current-potential curves for powdered standard samples obtained by linear sweep voltam-

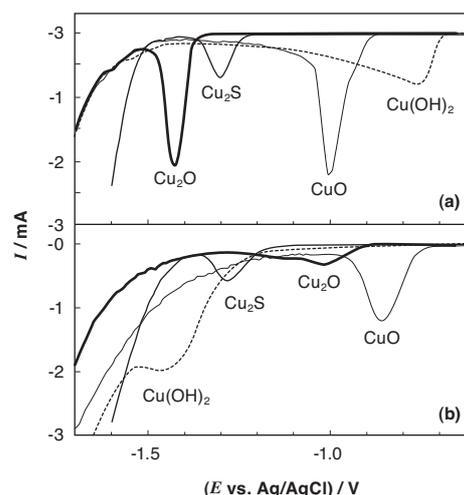


Fig. 2. Current-potential curves recorded by LSV for powder samples. Electrolyte solutions: (a) 6 M KOH + 1 M LiOH, (b) 0.1 M KCl. Scan rate: 10 mVs⁻¹.

metry (LSV). As shown in Fig. 2 (a), the reduction peak of Cu₂O is separated sufficiently with that of CuO. The reduction peak of Cu₂S is also separated with that of Cu₂O. On the other hand, the separation of each peak was ambiguous in a conventionally-used electrolyte of 0.1 M KCl.

For the study of quantitative performance of the new method, standardized samples (i.e., Cu|Cu₂O, Cu|CuO, Cu|Cu₂S) were prepared, followed by the verification of the analytical precision in light of other analytical methods. As a result of detailed investigation, simultaneous quantification of copper oxides and sulfides, which lead directly to tarnishing, became possible^{(15),(16)}. This new method has been applied for quantitative analysis of the layers around nm~μm of copper oxides and sulfides in our company.

The electrolyte of “6 M KOH + 1 M LiOH” played a significant role in sifting the reduction peak of Cu₂O to lower potential⁽¹⁴⁾. For the clarification of this specific behavior, EIS was applied.

Figure 3 (A)⁽¹⁸⁾ shows the electrochemical impedances of Cu|Cu₂O samples obtained by reducing Cu₂O at constant current density in 1 M of alkali hydroxide (i.e., LiOH, NaOH, and KOH). In every case, a large semi-circle appeared in the upper part of the complex plane. The diameter of the semi-circle in the high-frequency range can be recognized as the charge-transfer resistance (R_{ct}) for the reduction of Cu₂O. The diameter of the capacitive loop (i.e., R_{ct}) was the largest for LiOH and decreased in the order of LiOH > NaOH > KOH. Thus, it was shown that Li⁺ ions had a reducing effect on R_{ct} , i.e., an inhibitory effect on the reduction of Cu₂O. On the other hand, the electrochemical impedance of a Cu|CuO sample is hardly affected by the kind of alkali hydroxide. As also shown in Fig. 3 (A), a characteristic inductive loop was observed in the low-frequency range for most measurements. This loop probably indicates the existence of some reaction intermediate. In Fig. 3 (B), both the capacitive and inductive loops became much larger when the KOH concentration was increased above 6 M. Thus, although the solution alkalinity

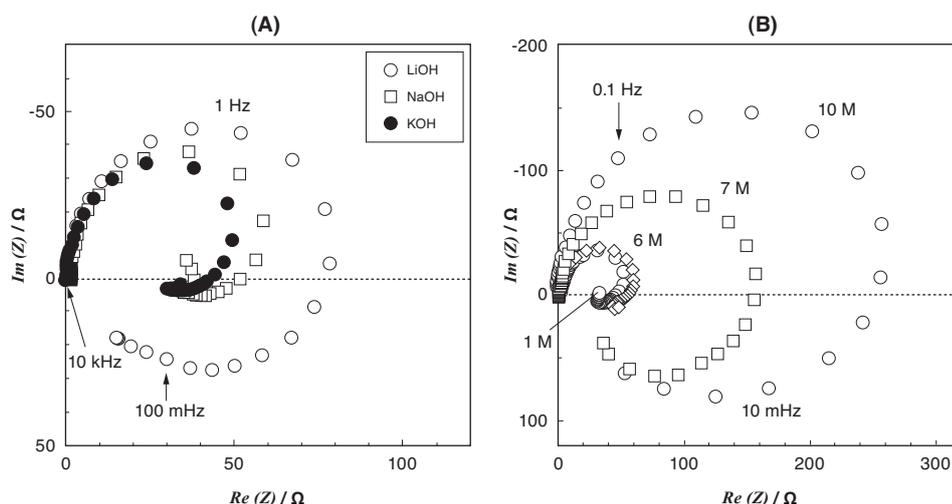


Fig. 3. Electrochemical impedance of Cu|Cu₂O samples in (A) 1 M LiOH, 1 M NaOH and 1 M KOH and in (B) various concentrations of KOH. DC: -1.0 mA. AC: 0.1 mA.

has a definite effect on the suppression of the Cu₂O reduction, Li⁺ ions should have a specific effect on it.

The corrosion of copper is accelerated when exposed to air containing moisture and pollutants. Figure 4⁽¹⁴⁾ shows the current-potential curves by LSV for copper sheets, which were previously oxidized by heating in a temperature/humidity-controlled chamber at 80°C and RH (relative humidity) 60% or 90%. Amounts of copper oxides formed on copper surfaces depended significantly on RH. That is to say, humidity control during shipping and storage is very important for the corrosion protection of copper. The desirable RH is within 40%.

In addition to the acceleration of copper corrosion depending on amounts of adherent ions on copper surfaces, different formation and growth mechanism of copper oxides was also clarified depending on species of those^{(22),(23)}. Moreover, after studying about the initial

oxidation of copper, we suggested the original mechanism⁽²⁴⁾.

2-2 Anodic polarization method⁽²⁵⁾

Metallic parts of the electronic component, such as contacts and connectors commonly consist of a substrate of copper with a thin layer of plated gold and often with a plated interlayer of nickel. That is, a trilaminar cross-section of Cu|Ni|Au is well known structure (Fig. 5). Flexible Flat Cable (FFC) is one of the most typical electronic component equipped in home electric appliances. Plated gold plays a corrosion protective role against an underlying metal. However, pore corrosion such as pinhole defects is a special type of bimetallic corrosion often observed on gold-coated electric contacts. In this corrosion, humidity and pollutants can penetrate through pinhole defects, and then less noble metal have possibility to be corroded selectively and rapidly. Therefore, the application of a quantitative analysis of pinhole defects in a gold-plated layer on nickel is of great importance for the quality control of the plating. However, it is difficult to obtain the average information of pinhole defects in large areas of the plating by ordinary instrumental analyses such as SEM (scanning electron microscope).

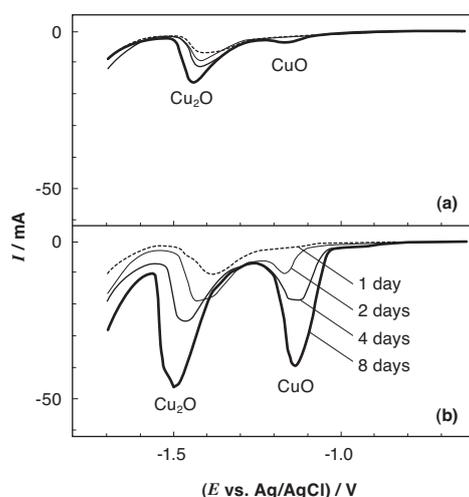


Fig. 4. Current-potential curves recorded by LSV for copper plates heated at (a) 80°C and RH 60% and at (b) 80°C and RH 90% for various times. Sweep rate: 100 mV s⁻¹.

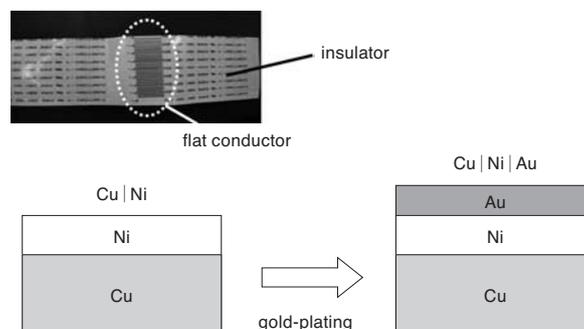


Fig. 5. Picture of FFC and schematic representation of gold-plating over nickel-plated copper substrate in FFC.

“Critical passivation current density method” (CPCD)^{(26),(27)} has been applied for the estimation of pinhole defects in thin films by dry coating, e.g., TiN and TiC on stainless used steel (SUS) substrates. The activated current depending on SUS was measured by polarizing the potential to anodic direction in an electrolyte such as “0.5 M H₂SO₄ + 0.05 M KSCN.” The ratio of pinhole defects are estimated quantitatively by making a comparison of the activated current peak between a real sample and SUS possessing a fixed surface area. CPCD is classified into “anodic polarization method” in terms of electroanalytical method. To my knowledge, there have been a few reports on the quantitative analysis of pinhole defects in plated layers. For the estimation of pinhole defects in a gold-plating layer of FFCs, the oxidation current, which depends on underlying nickel, is measured by an anodic polarization method. However, the peak current generated by using “0.5 M H₂SO₄ + 0.05 M KSCN” as an electrolyte was not large enough for detecting the very small pinhole defects. The optimization of the electrolyte focusing on sensitivity and quantitative performance was carried out, and then 5 M H₂SO₄ was concluded to be suitable as an electrolyte. The ratio of pinhole defects over 0.05% could be achieved. This new method ought to be available for a shipping inspection because the quality of gold-coated electric contacts can be determined quantitatively.

Figure 6 shows the anodic polarization curves for a gold foil, a nickel plate and a copper plate in 5 M H₂SO₄. In the range of measuring potential, gold gives no influence on the activated current of nickel.

Although pinhole defects in a gold-plated layer tend to decrease with an increase of the plating thickness, an excessive use of gold results in a cost problem. But generally, pinhole defects in a gold-plated layer decrease adequately when the qualities of a base nickel-plated layer are high enough⁽²⁸⁾. Therefore, the quantitative analytical method for the pinhole defects in a nickel-plated layer on copper substrates (i.e., Cu|Ni) was also of great importance for the precise quality estimation of nickel-plated layer.

In the structure of Cu|Ni before gold-plating, a plated metal is less noble than an underlying metal. As shown in **Fig. 6**, nickel is firstly oxidized in the process of the anodic polarization, followed by the oxidation of copper. It was found that the separation of the two-oxidation peaks was very difficult in sulfuric acids, since a real surface area of nickel exposed to an electrolyte was much larger than that of underlying copper in FFCs. The fundamental revision of the electrolyte was requisite for the separation of copper and nickel. As a result of further investigation, it was concluded that an alkaline solution was favorable as an electrolyte in this case. Nickel is a metal relatively resistant to an alkaline solution, whereas copper is easily oxidized to form copper oxides and a hydroxide⁽²⁹⁾. On the basis of the different feature each metal possesses, the optimization of an electrolyte was carried out. As shown in **Fig. 7**, the electrolyte of 7 M KOH allowed detecting the current peak due to the formation of a copper hydroxide without the interference of the anodic reaction of nickel. As a result of focusing on sensitivity and quantitative performance, the ratio of nickel pinhole defects over 0.01% could be achieved.

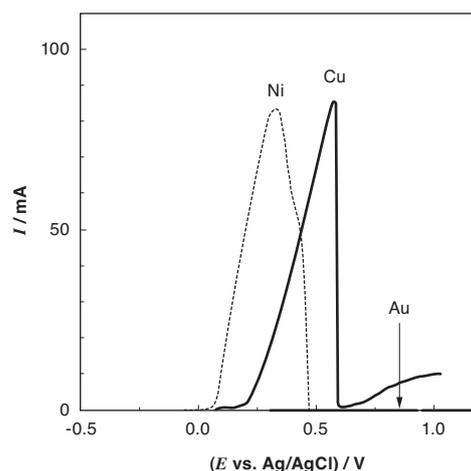


Fig. 6. Current-potential curves recorded by the anodic polarization method for gold foil (0.5 cm²) nickel plate (0.5 cm²) and copper plate (0.5 cm²) in 5 M H₂SO₄. Scan rate: 1 mVs⁻¹.

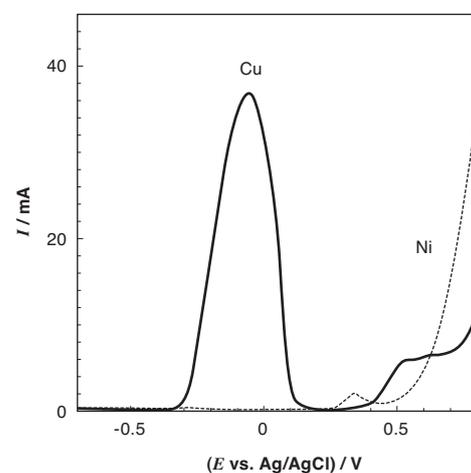


Fig. 7. Current-potential curves recorded by the anodic polarization method for nickel plate (0.5 cm²) and copper plate (0.5 cm²) in 7 M KOH. Scan rate: 100 mVs⁻¹.

2-3 Bromine addition method⁽³⁰⁾

Electroplated coatings of nickel are common, because the plating serves both corrosion protection and aesthetic functions.

For producing the bright plating, brightening agents, which classified first and second-order, are added into the plating bath. Saccharin and 2-butyne-1,4-diol (BD) have been frequently used as a first or a second-order brightening agent, respectively. Recently, sodium allylsulfonate (AS) possessing sulfonic and allylic groups has also been used. This agent has availabilities of both first and second-order⁽³¹⁾.

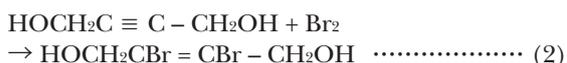
As concentration of each component in nickel-plating bath fluctuates momentarily with the operation times of the plating, decreased components require to be supplied on the basis of analytical values. However, in addition to the low concentration of “BD” in the plating bath,

a large portion of hydrogen generated at the plating is utilized for hydrogen addition to "BD"⁽³²⁾. Moreover, a result of analysis by some methods, such as liquid chromatography, is subject to principal components of nickel-plating solution, although "BD" containing no other component can be analyzed. From above mentioned restrictions, it has seemed to be difficult to determine "BD" in nickel-plating solution.

The method of "bromine addition" has been known as an old-established method for the determination of "BD"⁽³³⁾. However, this method is unsuitable for the control of a nickel-plating bath, because analytical precision is insufficient with nickel-plating solution⁽³⁴⁾. The reason of the poor precision seemed to be the use of liquid bromine, which is unstable and contains impurities. Distinct from existing methods, a "bromine addition" method using electrolytically generated bromine was investigated. In this method, bromine was obtained from a KBr solution before each analysis. Bromine can be generated with high current efficiency using an acidic solution that contains Br⁻ ions (see ref.(3), p161). By the detailed investigation, it became possible to determine 10-100 gm⁻³ of "BD" in a nickel-plating solution. The lower limit of around 5 gm⁻³ was achieved.

Key points of this new analytical method are; (1) the amounts of generated bromine according to Faraday's law, (2) the prevention of a loss of bromine under analytical operations and (3) the procedure of the enough reaction times for "bromine addition."

Apparatus shown in Fig. 8 were applied for a series of the operation. The reaction container was covered with "Parafilm" for the prevention of a loss of bromine. A conventional three-electrode electrolytic cell was employed for the generation of bromine (Eq. 1) using an apparatus of galvanostat. Eq. 2 means the "bromine addition" for triple bond of "BD."



A KI solution was continuously added into the solution containing unreacted bromine, and then iodine equivalent to the bromine was generated (Eq. 3). Finally, the iodine was titrated by a standard sodium thiosulfate solution (Eq. 4).

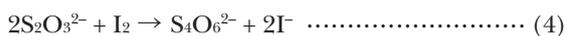


Figure 9 (a) shows the recovery of "BD" for the reaction time between 0.5 mg of "BD" and bromine generated at 20 mA for 5 min in 20 cm³ of a KBr solution. About 30 min was necessary for the complete reaction.

"BD" can be analyzed quantitatively when a series of the electrochemical reactions follows Faraday's law. However, a slight loss of bromine arose through the "bromine addition" in spite of the masking with "Parafilm." It took a blank test separately to gain the precise value⁽³⁰⁾.

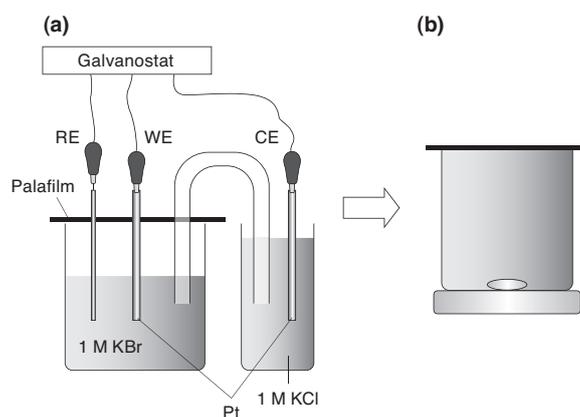


Fig. 8. Schematic representations of (a) electrolysis system for generation of bromine and (b) sample container after adding the nickel-plating solution.

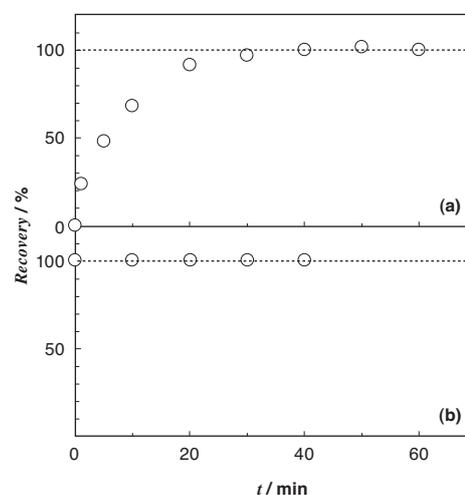


Fig. 9. Analytical values of "BD" or "AS" gained by electrolytically-generated "bromine addition" method for the reaction time. Sample solutions contain 50 gm⁻³ of (a) "BD" or (b) "AS."

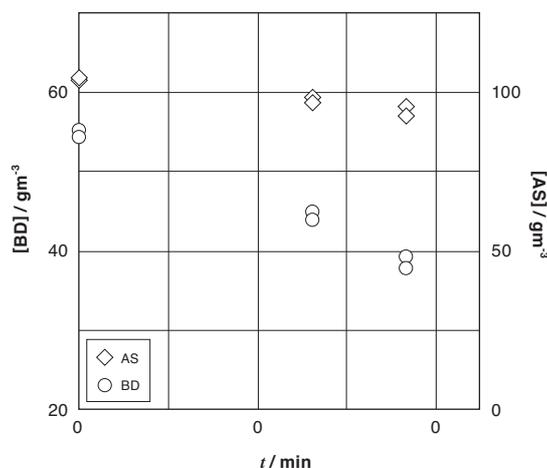


Fig. 10. Analytical values of "BD" or "AS" gained by electrolytically-generated "bromine addition" method for the operating time of the nickel-plating.

A serious issue came out in the course of the investigations. Although main components of the nickel-plating solution had no influence on this method, "AS" in the commercially available solution containing brightening agents elevated the quantitative value of "BD." Generally, it is difficult to determine some components separately by a titration method. However, further investigation revealed that "AS" reacted with bromine quantitatively and also rapidly as shown in Fig. 9 (b). There, the condition utilizing the different reaction time was applied, and then the selective determination of "BD" and "AS" became possible.

Figure 10 shows analyzed data of "BD" and "AS" for plating times in nickel-plating bath. Designed initial concentrations were 50 gm^{-3} for "BD" and 100 gm^{-3} for "As," respectively. This estimation was carried out to clarify the timing of the supply of the brightening agents because each agent was supposed to be transformed for different species in the operating time. It was clarified that the decomposition rate of "BD" was too rapid in comparison with that of "AS."

3. Conclusion

The recently developed three-electrochemical analyses were described.

(1) Voltammetry using strongly alkaline electrolyte

Around $\text{nm} \sim \mu\text{m}$ of copper oxides and sulfides could be determined quantitatively. The separation of the reduction peaks was very clear in comparison with conventional methods.

(2) Anodic polarization method

Quantitative analyses of pinhole defects in plated layer of FFC were developed. The ratio of pinhole defects over 0.05% in a gold-plated layer and over 0.01% in a nickel-plated layer could be evaluated.

(3) Bromine addition method

$10\text{-}100 \text{ gm}^{-3}$ of "BD" in nickel plating solution could be determined by the method of adding electrolytically-generated bromine. The presence of "AS" elevated the quantitative values of "BD," however, selective determination of "BS" and "AS" became possible by using different reaction times for "bromine addition."

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