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| Citation | 北海道大學工學部研究報告, 132, 41-47 |
| Issue Date | 1986-07-31 |
| Doc URL | https://hdl.handle.net/2115/42008 |
| Type | departmental bulletin paper |
| File Information | 132_41-48.pdf |

北海道大学工学部研究報告
第132号（昭和61年）

Bulletin of the Faculty of Engineering,
Hokkaido University. No.132 (1986)

# The Effect of a Powdery Copper Layer on the Electrolysis of Dilute Cupric Sulfate Solution in a Stacked Rotating Bipolar Electrode Cell

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(Received March 31, 1986)

## Abstract

The effect on the rate of electrolysis of a predeposited powdery copper layer on the electrodes in a stacked rotating bipolar electrode cell was studied in dilute cupric sulfate solutions. Polarization curve measurements and the electrolysis of 30 1 of 100 or 500 ppm $Cu^{2+}$ solutions were carried out with electrodes covered with powdery copper layers formed under various conditions.

The rate of electrolysis is promoted remarkably by the powdery copper and the higher speed is attributed to increases in surface micro-turbulence with increases in the active surface area. It is concluded that a powdery copper layer predeposited on electrodes enables high speed electrolysis, and the optimum pre-electrolysis conditions for the layer are proposed.

## 1. Introduction

A stacked rotating bipolar electrode cell was developed for recovery of heavy metals from dilute solutions. The structure of the cell and the characteristics in electrolysis of dilute cupric sulfate solution were presented elsewhere.[1] A high recovery speed is attained due to the excellent stirring effect of the rotating electrodes and the speed is further promoted by the deposition of powdery copper.

In this work the effect on the electrolysis rate of a powdery copper layer on the electrode is studied, and the pre-electrolysis conditions for preparing the layer are examined.

## 2. Experimental

The stacked rotating bipolar electrode cell in this work, consists of two feeder electrodes and four stator bipolar electrodes alternating with five rotor bipolar electrodes, and is described in detail elsewhere.[1] The electrodes are disks of about 6cm diameter and 6mm thickness, and acrylic fins are mounted on the anode surfaces to promote turbulence and scrape of the deposited copper.

Polarization curves were measured on the cathode in a single cell with one rotor and two stator electrodes; the electrode size and inter-electrode gaps are as in the above cell. The

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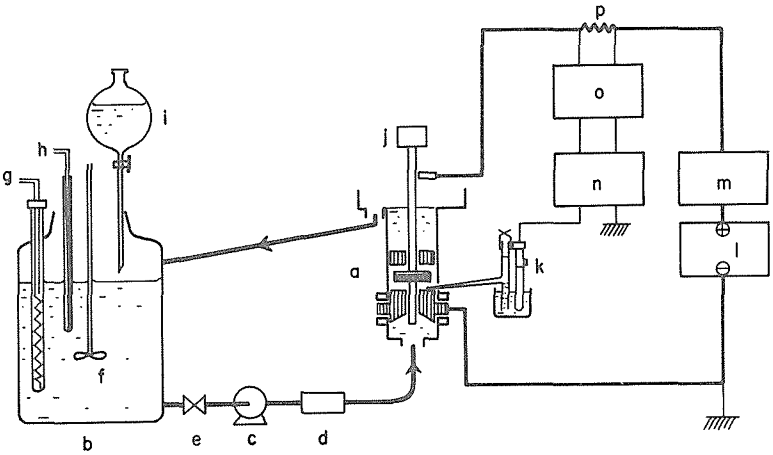

**Fig. 1** Apparatus and measurement system for polarization curves. a = test cell, b = reservoir tank, c = pump, d = flow meter, e = valve, f = impeller, g = heater, h = thermocouple, i = 1 M $CuSO_4$ solution, j = motor, k = Ag − AgCl electrode, l = power supply, m = coulommeter, n = high impedance voltmeter, o = recorder, p = standard resistance.

measurements were carried out in 100 ppm and 500ppm $Cu^{2+}$ solutions on electrodes covered with predeposited copper layers. The layers were prepared at various potentials and electricity amounts in solutions similar to the test solutions; 1M cupric sulfate solution was added continuously to keep the concentration constant. The apparatus and the measurement system is presented in Fig.1. The potential was referred to an Ag-AgCl electrode. The rotation speed, $\omega$, was 700rpm and the flow rate of the solution, Q, circulating between the cell and a reservoir was 3.4 1 $min.^{-1}$

Electrolysis of 30 1 solution from 500 to 100 ppm $Cu^{2+}$ and from 100 to 10ppm $Cu^{2+}$ were carried out with the stacked rotating bipolar electrode cell at various constant currents. The flow rates of the electrolytes were 3.4 1 or 5.0 1 $min.^{-1}$ and other conditions are similar to those of polarization curve measurements. The electrolysis was carried out with constant currents; the cell voltage, Vcell (V) , current,J (A) , and quantity of electricity were measured. The variation in $Cu^{2+}$ concentration was followed by atomic absorption spectrophotometry, where small samples of electrolyte were withdrawn from the reservoir when specific quantities of electricity had been consumed.

## 3. Results and discussion

Steady state polarization curves on smooth copper surfaces are presented in Fig.2. The broken curve here is obtained by subtraction of the curve with copper free solution from that of 100 ppm $Cu^{2+}$ solution,and it shows a plateau from about −0.7 to −0.2 V. The curve in the copper free solution shows that oxygen reduction takes place below about −0.2 V and hydrogen evolution below about −0.7 V. Therefore the polarization curve of the 100 ppm $Cu^{2+}$ solution can be interpreted as follows: the curve rises steeply from a few tens of millivolts for copper deposition and via a plateau, rises again from about −0.7 V due to

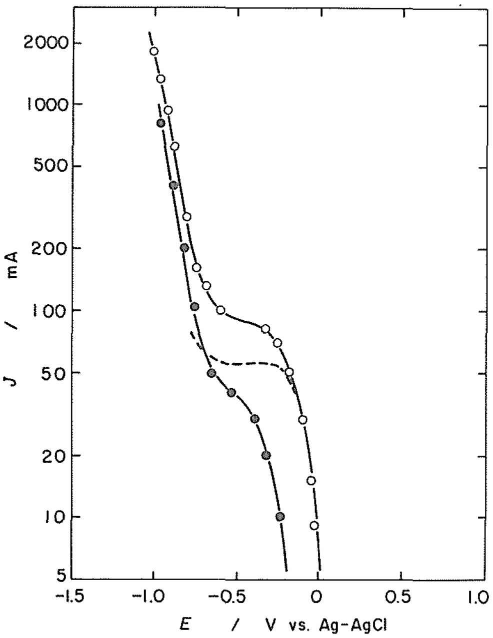

**Fig. 2** Polarization curves on smooth copper electrode. $\omega = 700$ rpm, $Q = 3.4$ l min.$^{-1}$ ○ = 100 ppm $Cu^{2+}$ with $5 \times 10^{-2}$ M $H_2SO_4$, and ● = $5 \times 10^{-2}$ M $H_2SO_4$ only.

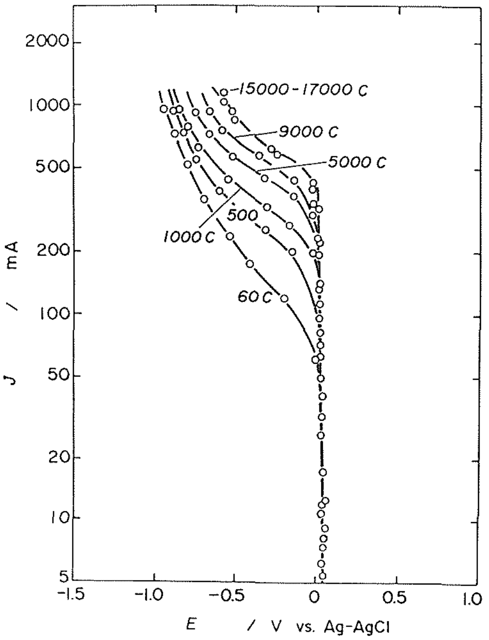

**Fig. 3** Polarization curves at various quantities of electricity for pre-electrolysis at $-0.25$ V in 100 ppm $Cu^{2+}$ solutions. $\omega = 700$ rpm, $Q = 3.4$ l min.$^{-1}$

hydrogen evolution. The plateau current is due to diffusion of cupric ions and does not show a definite constant value since oxygen reduction takes place simultaneously. From the plateau of the broken curve, the diffusion limiting current of copper is estimated to be about 55 mA.

When prolonged cathodic polarization is carried out near or at the diffusion limiting current of copper ions, copper deposits are powdery and copper deposition and hydrogen evolution increases. To investigate the role of the powdery copper in the increase in activity, electrolysis to deposit a powdery copper layer was carried out under various conditions, and polarization curves were measured.

Polarization curves for various quantities of electricity with pre-electrolysis at $-0.25$ V are presented in Fig.3. The figure shows that the activity increases with the increase in the electricity consumed and eventually reaches a maximum value at 15000 coulombs, above which it is approximately unchanged.

Fig.4 shows examples of polarization curves at the maximum activity and the dependence on the pre-electrolysis potential. The quantity of electricity of the pre-electrolysis is in the range 7000 to 18000 coulombs. As seen from the figure the maximum activity is little sensitive to the pre-electrolysis potential.

Some of the powdery copper deposits remain on the electrode during the electroysis, while at the same time a part is removed by the rotation of the electrode and the electrolyte flow. In the early stage of electrolysis, most of the deposited copper probably remains while the removal increases with the time of electrolysis. The maximum activity is achieved,

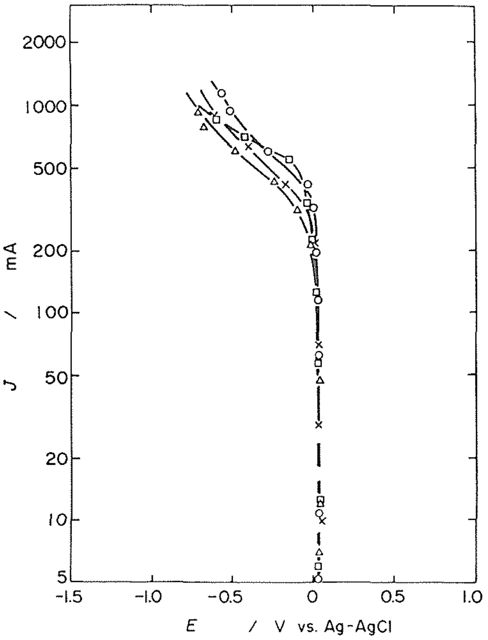

**Fig. 4** Polarization curves for various electrodes with pre-electrolysis in 100 ppm $Cu^{2+}$ solution. $\omega = 700$ rpm, $Q = 3.4$ l · $min.^{-1}$ Pre-electrolysis potential(V/vs. Ag−AgCl): △ = −0.14, × = −0.20, ○ = −0.25, and □ = −0.40.

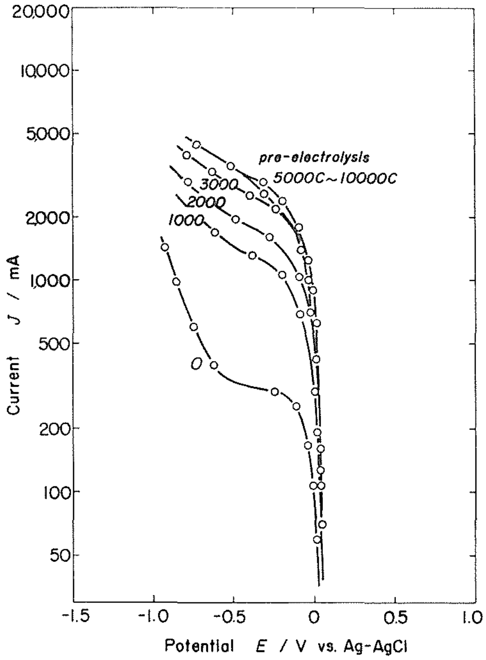

**Fig. 5** Polarization curves at various quantities of electricity for pre-electrolysis at about −0.25 V in 500 ppm $Cu^{2+}$ solution. $\omega = 700$rpm, $Q = 3.4$ l · $min.^{-1}$

when a saturated deposit roughness has been attained, as in the rotating cylinder electrode.[2] The reproducibility of the electrode activity for the same quantity of electricity is not always good, because of the instability of the accumulated copper layer which is being formed and swept off simultaneously.

Polarization curves at various quantities of electricity for pre-electrolysis in 500 ppm $Cu^{2+}$ solution are presented in Fig.5. The pre-electrolysis was carried out galvanostatically by a stepwise increased current, with increases in the quantity of electricity as shown in scheme 1 in Table 1; Fig.5 shows that the set up potential for the pre-electrolysis is about −0.25 V. The activity increases with the increase in the quantity of electricity for pre-electrolysis such as in Fig.3; the electrodes here reach maximum activity in the range above 5000 coulombs.

To observe the surface morphology of the deposits, copper deposits on an electrode were prepared carefully to avoid disturbing the structure of the deposit, and this was

Table 1 Pre-electrolysis schemes with 500ppm $Cu^{2+}$ solution.

| scheme 1 | | scheme 2 | |
|---|---|---|---|
| quantity of electricity (coulomb) | current (A) | quantity of electricity (coulomb) | current (A) |
| 0 | 1.0 | 0 | 0.2 |
| 1000 | 1.5 | 120 | 0.5 |
| 2000 | 2.0 | 1000 | 0.75 |
| 3000 | 2.5 | 2000 | 1.0 |
| 5000 | 2.25 | 3000 | 1.25 |
| 10000 | | 4000 | 1.5 |
| | | 5000 | 1.75 |
| | | 7000 | 2.0 |
| | | 10000 | |

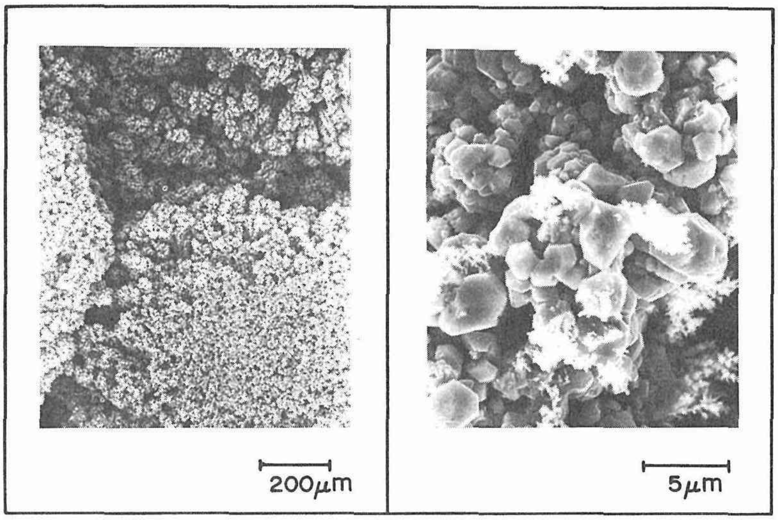

**Photo. 1** SEM photographs of surface of deposited copper at $-0.14$ V and 25000 coulombs.

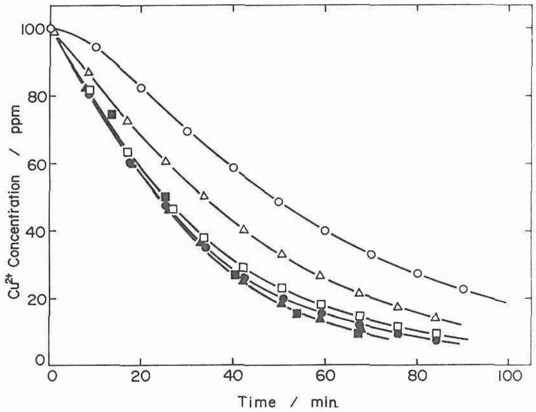

**Fig. 6** *Concentration variation with time in* 30 1 of 100 ppm $Cu^{2+}$ solution with various pre-electrolyzed electrodes. $J=0.5$ A, $\omega=700$ r.p.m., Q 3.4 1 $min.^{-1}$ The quantity of electricity for the pre-electrolysis (coulomb): ○=0, △=1000, □=2000, ●=3000, ▲=6000, and ■=10000.

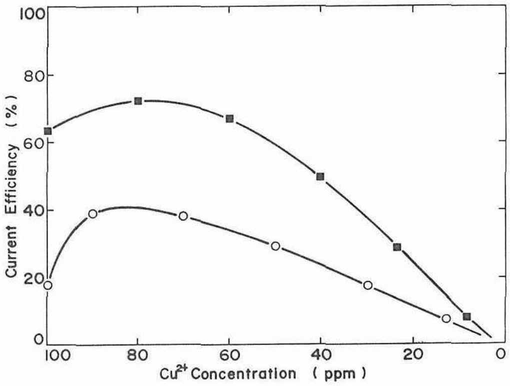

**Fig. 7** *Current efficiency variations with* $Cu^{2+}$ concentration on different pre-electrolyzed electrodes. $J=0.5$ A, $\omega=700$ rpm, $Q=3.4$ 1 $min.^{-1}$ The quantity of electricity for pre-electrolysis(coulomb): ○=0, and ●=10000.

observed under a scanning electron microscope. Photo 1 shows SEM photographs of the layer formed at $-0.14$ V and 25000 coulombs. The layer is composed of hills and valleys about 1 mm in diameter. Each hill has a complex structure of crystals of micron size.

The equivalent Nernst diffusion layer thickness calculated from the diffusion limiting current in Fig.2 is about 8 $\mu$m on a smooth surface at 700 rpm and 3.4 1 · $min.^{-1}$ Considering the profile of the layer and the diffusion layer thickness the increase in activity by the deposited copper can be attributed to the increased surface micro-turbulence and a marked increase in active surface area.[2,3]

To examine the effect on the accumulated deposits of the time taken to recover copper from a dilute solution, electrolysis was carried out with various pre-electrolyzed electrodes with 30 1 of 100 ppm $Cu^{2+}$ solution, and the results are shown in Fig.6. The time for the electrolysis decreases with the increase in the quantity of electricity for the pre-electrolysis and reaches a minimum above 6000 coulombs. The minimum electrolysis time is about half of that the electrodes without pre-electrolysis with initially smooth surfaces. As the electrolysis proceeded, the surface gradually became rough with accumulation of copper.

When the roughness of the smooth electrode is unchanged during electrolysis, the minimum time needed for electrolysis with a smooth surface can be calculated from the mass transfer coefficient, and to estimated as $8.6\times10^{-3}$ cm · $s^{-1}$ from the diffusion limiting current mentioned above. The time of electrolysis from 100 to 10 ppm for 30 1 of $Cu^{2+}$ solution becomes about 640 minutes and is about ten times that of the minimum electrolysis time with pre-electrolyzed electrodes. This clearly shows that roughening the electrode surface by depositing powdery copper speeds up the electrolysis of dilute solution as was expected from the polarization curves.

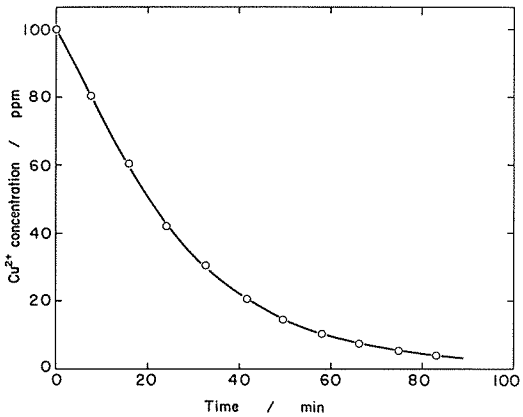

**Fig. 8** Concentration variation with time in 30 1 of 100 ppm $Cu^{2+}$ solution with pre-electrolysis as schem 2 in Table 1. J=0.5 A, $\omega$= 700 rpm, Q=3.4 1 · min.$^{-1}$

The high speed that is achieved by roughening the electrode surface is due to the high current efficiency as can be seen from Fig.7. The figure shows current efficiency variations with $Cu^{2+}$ concentration on different pre-electrolyzed electrodes. The current efficiency with the roughened electrode is about 70% from 100 to about 60 ppm whereupon it gradually decreases. The decrease in current efficiency is initially due to oxygen reduction and is accelerated by hydrogen evolution as the concentration decreases. Electrodes without pre-electrolysis show very low current efficiency at all concentrations, because hydrogen evolution takes place from the initial stage of electrolysis.

Table 2 Characteristics of the stacked rotating bipolar electrode cell pre-electrolyzed as scheme 2 in Table 1 in the electrolysis of 30 1 solution. $w$=700rpm, $Q$=5.0 1·min$^{-1}$.

| Concentration (ppm) | J (A) | t (min) | Vcell (V) | $\bar{\eta}$ (%) | W (kwh/kg) |
|---|---|---|---|---|---|
| 500 → 100 | 2.0 | 44 | ca. 57 | 67 | 7.2 |
| 100 → 10 | 0.4 | 66 | ca. 30 | 53 | 4.8 |

Concentration changes with time on the powdery copper layer prepared using scheme 2 in Table 1 are presented in Fig.8. The set up potential for the pre-electrolysis was about −0.1 V and the formed layer is firmer than that prepared by scheme 1 at −0.25 V. Comparing this curve with the curve in Fig.6, which shows minimum electrolysis times, shows that the time needed for electrolysis from 100 to 10 ppm is reduced by about 9 minutes, although the maximum activity is nearly insensitive to the pre-electrolysis potential as shown in Fig.4. The pre-electrolysis layer in scheme 1 may became upset or partly break up when replacing pre-electrolysis electrolyte with test electrolyte. Thus it is desirable that the pre-electrolysis layer is somewhat firm and the scheme 2 in Table 1 is advantageous in the present work.

Some characteristics of the stacked rotating bipolar electrode cell with electrodes prepared using scheme 2 are presented in Table 2; t(min.) is the time for the electrolysis, $\bar{\eta}$(%) is the average current efficiency, and W(kwh $kg^{-1}$) is the power consumption.

The times are remarkably short and the average current efficiency is high in both concentration ranges. These results are attribute to the excellent stirring effect of the fins on the electrode and the increase in surface micro-turbulence with the increase in the active surface area caused by the powdery copper.

The energy consumption is low for both ranges, but from 500 to 100 ppm it is higher than from 100 to 10 ppm due to the high cell voltage. A large portion of the cell voltage in the high concentration range is from the ohmic potential drop brought about by electrolyzing with a high current density in an electrolyte of low electric conductivity. This is often the case when electrolyzing dilute solutions without supporting electrolyte as used here.

## 4. Conclusions

The rate of electrolysis in the stacked rotating bipolar electrode cell is promoted remarkably by deposited powdery copper. The increased speed is attributed to the increased surface micro-turbulence with an increased active surface area.

High speed electrolysis is achieved with predeposition of a powdery copper layer on the electrode, and it is desirable that this pre-electrolysis layer is somewhat firm. Scheme 2 in Table 1 is advantageous as the pre-electrolysis condition.

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