

## THE EFFECTS OF ULTRASOUND ON CATHODIC AND ANODIC ELECTRODE REACTIONS IN ACID COPPER SYSTEMS

**K. Kobayashi, A. Chiba, K. Tsuzuki, and H. Okada**

Department of Materials Chemistry, Yokohama National University, JAPAN  
kat-koba@ynu.ac.jp

### Abstract

In the acid copper sulfate electrolytes, the imposition of ultrasound led to the negative shifts of both the equilibrium potential,  $E_{eq}$ , and the potential of inflection point on current-overpotential curve,  $E_{inf}$ , separated from  $E_{eq}$ . When the potentials stepped from  $E_{eq}$  were positive or negative relative to  $E_{inf}$ , the cathodic stationary current after potential-step decreased or increased with ultrasonic irradiation, respectively. The anodic stationary current after potential-step increased at every stepped potential with irradiation. The results on faradaic impedance measurements showed that the ultrasonic irradiation accelerated the rates of charge transfer reactions on both the cathodic and the anodic processes and increased the capacitance of the double layer at the metal-electrolyte interface. The imposition of ultrasound may decrease the thickness of the double layer, so that the potential at the outer Helmholtz plane may be energetic to accelerate both cathodic and anodic charge transfer processes.

### Introduction

In sonoelectrochemistry, the effects of ultrasonic irradiation on mass transport processes in reversible electrochemical systems have been widely reported [1, 2]. However we recently reported that the imposition of an ultrasound accelerated charge transfer processes in electroplating systems of nickel [3] and copper [4], the mechanism of contributions of ultrasound to charge transfer processes has not been elucidated in detail.

A potential-step chronoamperometry, PSCA, and a faradaic impedance method, FI, are electrochemical methods suitable to exhibit the transient of the rate of charge transfer reaction and the change of structure of metal-electrolyte interface immediately after an imposition of ultrasound. The present study reports about the effects of ultrasonic irradiation on both charge transfer processes and interfacial structures in acid copper sulfate electrolytes by various electrochemical methods.

### Experimental

The compositions of electrolytes on acid copper electrochemical systems were (0-0.5) M  $\text{CuSO}_4$  + (0.1-5.0) M  $\text{H}_2\text{SO}_4$ . A working electrode (WE) was of 5 mm diameter copper rod (purity 99.99%) imbedded into teflon tubing and the exposed top plane (0.20  $\text{cm}^2$ ) was set apart by 2 mm just under the head

(1.3 cm diameter) of horn chip of ultrasonic transducer (Shimazu USP-400A, 20 kHz, 400 W). A power of ultrasonic irradiation was changed to (10-70) %, and a period of irradiation (0.5-3) ms, and a duty ratio during irradiation 0.5-1.5. A platinum wire or a copper rod was used as a counter electrode and an Ag/AgCl reference electrode in saturated KCl solution was connected to cell with salt bridge separated by a chip of vycol glass.

Direct current (d.c.) polarization measurements were mainly carried out at 10 mV/s of scan rate with a potentiostat (Fuso 1100L) and a function generator (Fuso HECS-321). In PSCA, a transient converter (Riken Denshi TCFL-8000) was used in addition to d.c. polarization equipments stated above and 8192 points of current data were sampled at (0.3-3) ms of sampling time. FI was carried out with 10 mV<sub>rms</sub> of a sinusoidal voltage from 100 Hz to 20 kHz using a frequency response analyzer (NF Electronic Instrument S-5020) and a personal computer (NEC PC-9801VM2).

After WE was polished with #2000 emery paper, dipped for several seconds in a dilute  $\text{HNO}_3$  solution and washed with water, it was set in electrochemical cell. The electrolytes were fully deaerated by bubbling with nitrogen and the bath temperature was controlled at (298 ± 5) K.

### Results and Discussion

#### *Polarization curves of acid copper electroplating system*

Figure 1a, the current-potential curve shows a typical one obeying Butler-Volmer equation where  $E_{inf}$  equals to  $E_{eq}$  (94 mV) and a cathodic transfer coefficient,  $\alpha_c$ , is smaller than 0.5. When an ultrasound was imposed,  $E_{eq}$  shifted to a negative potential (80 mV) and  $E_{inf}$  appeared at a potential (46 mV) more negative by several tens of mV than  $E_{eq}$ . The value of the cathodic current (-1 mA) at  $E_{inf}$  can't be entirely explained with consideration of the charging current in the double layer. The imposition of ultrasound increased both cathodic and anodic currents except the narrow potential region near  $E_{eq}$ . Figure 1b shows a typical anodic polarization curve in the case of a periodical imposition of ultrasound. It is clear that an ultrasonic irradiation accelerates the rate of charge transfer of copper. The values of the anodic rate constant and the transfer coefficient obtained from Tafel plots of anodic polarization curve

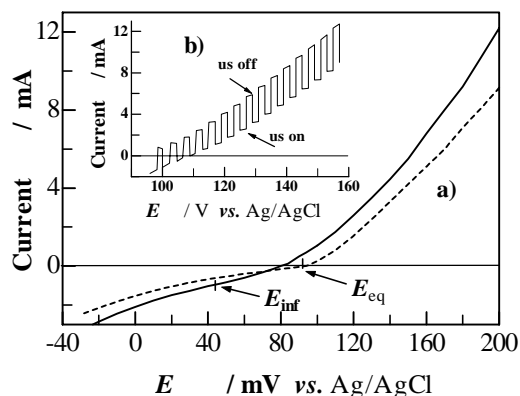


Figure 1: Effects of ultrasonic irradiation on polarization of Cu in 0.5 M CuSO<sub>4</sub> + 0.5 M H<sub>2</sub>SO<sub>4</sub>. a) A solid line and broken line are data with irradiation and without irradiation, respectively. b) Duration with and without irradiation were 1 s and 1 s. 40% of a power was irradiated

with ultrasonic irradiation were  $1.4 \times 10^{-4}$  cm/s and 0.39, while those without irradiation were  $1.1 \times 10^{-4}$  cm/s and 0.35, respectively. The values of anodic rate constant were larger than values of  $5.2 \times 10^{-5}$  cm/s with irradiation and  $6.1 \times 10^{-6}$  cm/s without irradiation measured on cathodic polarization [4].

*PSCA of acid copper electroplating system*

Figure 2 shows the typical current transients measured with PSCA and Figure 3 shows stationary currents at every stepped potential before and after an imposition of ultrasound. On cathodic polarization, the effects of ultrasonic irradiation on cathodic

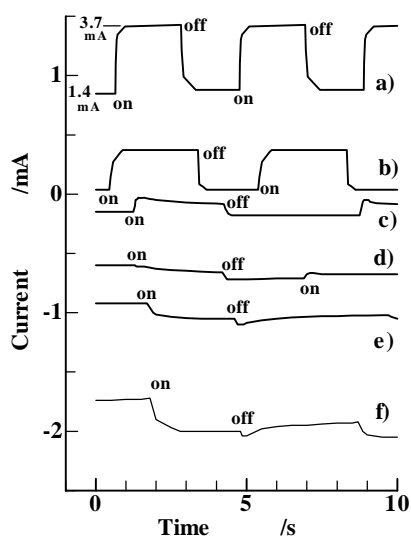


Figure 2: Current transients of PSCA with and without ultrasonic irradiation in 0.5 M CuSO<sub>4</sub> + 0.5 M H<sub>2</sub>SO<sub>4</sub>. The stepped potentials were a) 125 mV, b) 100 mV, c) 70mV, d) 15 mV, e) 0 mV, and f) -30 mV.

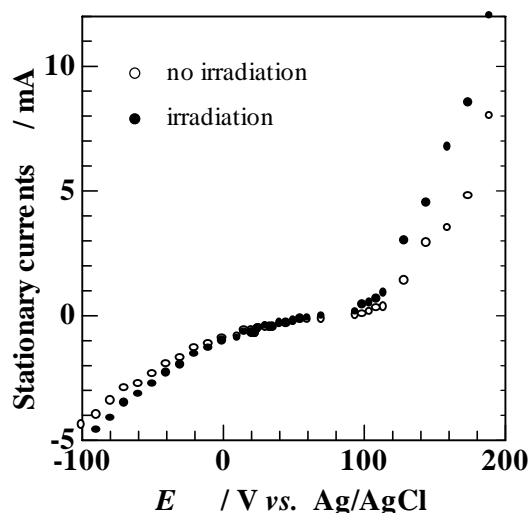


Figure 3 : Stationary currents of PSCA with and without ultrasonic irradiation in 0.5 M CuSO<sub>4</sub> + 0.5 M H<sub>2</sub>SO<sub>4</sub>.

currents changed from promotion at negative potentials more than  $E_{inf}$  to depression (Figure 2c) at positive potentials more than  $E_{inf}$ . On anodic polarization, the imposition of ultrasound increased anodic currents, though the effects of ultrasonic irradiation were not almost observed at overpotentials beyond 0.2 V (the results is not shown in Figure). Table 1 shows the ratio of anodic stationary currents with irradiation to those without irradiation. The less became the anodic overpotential, the promotion effects of ultrasonic irradiation became the larger. Those results suggest that the imposition of ultrasound increases cathodic or anodic partial currents at negative or positive potentials more than not  $E_{eq}$  but  $E_{inf}$ , respectively. It is probable that in the vicinity of  $E_{eq}$ , anodic reactions with irradiation is already under a large overpotential relative to  $E_{inf}$ , while anodic reactions without irradiation is still under a small overpotential relative to  $E_{eq}$ . Namely, the ratio of the former to the latter was large in the vicinity of  $E_{eq}$ , while the ratio for currents became small as the ratio for overpotentials of the former to the latter became small in the region of overpotentials beyond 0.2 V.

*Determination of electrochemical parameters by faradaic impedance method*

Kinetic and interfacial parameters on the acid copper sulfate system were determined from faradaic impedance measurements. Figure 4 shows the impedance plots on cathodic polarization. In potential region more negative than  $E_{inf}$ , shown in Figure 4c) and 4d), the more negative were the electrode potentials,  $E$ , the values of the charge transfer resistance,  $R_{ct}$  which is defined as the diameter of the circle on impedance plots [3], became the smaller, and the promotion effect for cathodic

Table 1 : Effects of ultrasound on anodic stationary currents measured with PSCA.  $I_{on}$  and  $I_{off}$  currents with and without ultrasound, respectively.

| Overpotential /mV | $I_{on}$ /mA | $I_{off}$ /mA | ratio |
|-------------------|--------------|---------------|-------|
| 5                 | 0.4          | 0.07          | 5.7   |
| 10                | 0.5          | 0.17          | 2.7   |
| 15                | 0.65         | 0.3           | 2.4   |
| 20                | 0.9          | 0.35          | 2.6   |
| 35                | 3.0          | 1.4           | 2.1   |
| 50                | 4.5          | 2.9           | 1.6   |
| 65                | 6.8          | 3.5           | 1.9   |
| 80                | 9.5          | 4.8           | 1.6   |
| 95                | 12           | 8.0           | 1.5   |
| 120               | 12           | 9.0           | 1.3   |
| 150               | 18           | 15            | 1.2   |
| 200               | 23           | 21            | 1.1   |

reaction with ultrasonic irradiation became the stronger. On impedance plots at 50 mV near  $E_{inf}$  the effects of imposition of ultrasonic irradiation is not clear. At 70 mV between  $E_{inf}$  and  $E_{eq}$ , the value of impedance was large and the value of  $R_{ct}$  obtained with irradiation was larger than that without irradiation. Table 2 shows the current densities measured with FI on anodic processes of copper in concentrations of 0.1 M and 1 M sulfuric acid. The anodic current densities in 1 M  $H_2SO_4$  were larger than 0.1 M  $H_2SO_4$ . In 0.1 M  $H_2SO_4$ , as the electrode potential became more positive than  $E_{eq}$ , the anodic current densities without irradiation increased linearly,

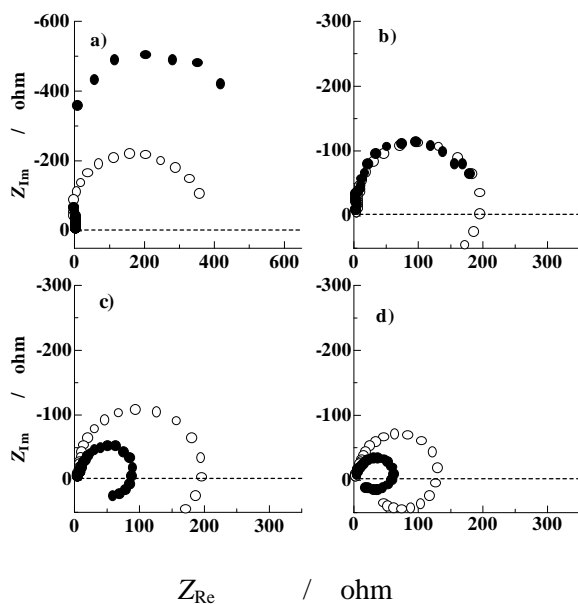


Figure 4: Impedance plots on cathodic polarization in 0.5 M  $CuSO_4$  + 0.5 M  $H_2SO_4$  with and without irradiation. Electrode potentials were kept at a) 70 mV, b) 50 mV, c) 30 mV, and d) -20 mV.  $\circ$  : no irradiation  $\bullet$  : irradiation

Table 2: Effects of ultrasonic irradiation on anodic current densities measured with FI. Off : without irradiation, on : with irradiation

| $E$ / mV | Anodic current density / $Acm^{-2}$ |     |        |               |     |        |
|----------|-------------------------------------|-----|--------|---------------|-----|--------|
|          | 0.1 M $H_2SO_4$                     |     |        | 1 M $H_2SO_4$ |     |        |
|          | off                                 | on  | on/off | off           | on  | on/off |
| 90       | 0.84                                | 2.1 | 2.5    | 4.4           | 9.1 | 2.1    |
| 100      | 1.9                                 | 3.9 | 2.1    | 6.0           | 14  | 2.3    |
| 110      | 2.6                                 | 5.0 | 1.9    | 8.4           | 15  | 1.8    |
| 120      | 3.6                                 | 6.2 | 1.7    | 12            | 18  | 1.5    |
| 130      | 4.4                                 | 7.1 | 1.6    | 15            | 27  | 1.8    |
| 140      | 4.9                                 | 7.8 | 1.6    | 18            | 34  | 1.9    |
| 150      | 6.1                                 | 8.9 | 1.5    | 22            | 45  | 2.0    |
| 160      | 7.2                                 | 12  | 1.7    | 26            | 51  | 2.0    |
| 170      | 7.9                                 | 12  | 1.5    | 30            | 34  | 1.1    |
| 180      | 8.8                                 | 16  | 1.8    | 35            | 41  | 1.2    |
| 190      | 8.8                                 | 20  | 2.3    | 38            | 41  | 1.1    |
| 200      | 9.9                                 | 27  | 2.7    | 47            | 51  | 1.1    |

while those with irradiation increased progressively. However the effects of ultrasonic irradiation on anodic current densities in 1 M  $H_2SO_4$  were almost constantly twofold, the promotion effect for anodic processes rapidly disappeared beyond 170 mV. From measurements with a potential sweep method, it has been certified that the polarization curve with irradiation agreed with that without irradiation beyond 250 mV, though the data are not displayed. Figure 5 shows the effects of ultrasonic irradiation on differential capacitances,  $C_{dl}$ , in 0.1 M and 1 M  $H_2SO_4$ . As the electrode potentials became more positive than  $E_{eq}$  and the concentration of  $H_2SO_4$  became large, the values of  $C_{dl}$  increased. Those behavior on values of  $C_{dl}$  is expected from the Gouy-Chapman theory as

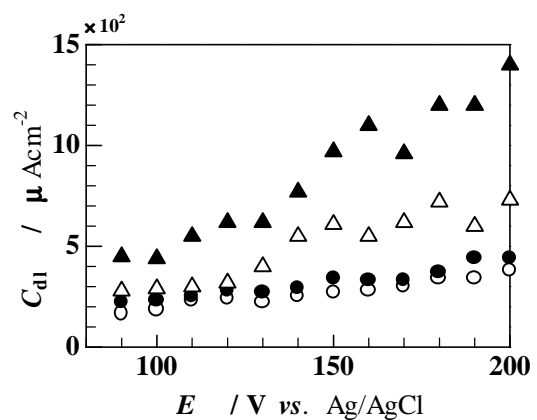


Figure 5: Effects of ultrasonic irradiation on differential capacitances in 0.1 M and 1 M  $H_2SO_4$ .  $\triangle$  : 0.1 M  $H_2SO_4$ ,  $\circ$  : 1 M  $H_2SO_4$ . Open and closed marks are used without and with irradiation.

the potential of zero charge of Cu electrode in H<sub>2</sub>SO<sub>4</sub> solution is about -0.16 V [5]. The imposition of ultrasound in the acid copper electroplating systems [4] and in the sulfuric acid solution increased in the values of  $C_{dl}$  as shown in Figure 5. The increasing in the values of  $C_{dl}$  with irradiation was marked in high concentrations of H<sub>2</sub>SO<sub>4</sub>. It is strongly suggested that the imposition of ultrasound caused partially the release of the water molecules solvated around the cations of copper or adsorbed on copper electrode by effects of a cavitation or a hammer-jet with ultrasonic irradiation. In such a case, the redox ions on the charge transfer processes can approach closely the electrode surface, so that the thickness of the double layer may decrease and the values of  $C_{dl}$  may increase.

The potential at the outer Helmholtz plane may be energetic to accelerate both cathodic and anodic charge transfer processes. The negative shifts of  $E_{eq}$  and  $E_{inf}$ , and the separation of  $E_{inf}$  from  $E_{eq}$  with the imposition of ultrasound may be interpreted by the detailed clarification of interfacial structures.

### Conclusions

In the acid copper electroplating systems, the imposition of ultrasound led to the increases in the rates of both cathodic and anodic charge transfer reactions. The negative shifts of both  $E_{eq}$  and  $E_{inf}$  separated from  $E_{eq}$  with the ultrasonic irradiation were confirmed with measurements by a potential sweep method and PSCA. From faradaic impedance measurements, the promotion effects of ultrasonic irradiation on the rates of cathodic and anodic charge transfer reactions were also confirmed. The anodic reactions of copper in the sulfuric acid solution were accelerated with an ultrasonic irradiation. The imposition of ultrasound markedly increased the capacitance of the double layer at the metal-electrolyte interface in high concentration of H<sub>2</sub>SO<sub>4</sub>. The imposition of ultrasound may decrease the thickness of the double layer, so that the potential at the outer Helmholtz plane may be very energetic to accelerate both cathodic and anodic charge transfer processes.

### References

- [1] J.C. Ball and R.G. Compton, "Application of ultrasound to electrochemical measurements and analyses," *Electrochemistry*, vol. 67, pp. 912-919, 1999.
- [2] K. B. Holt, J. D. Campo, J. S. Foord, and R. G. Compton, and F. Marken, "Sonochemistry at platinum and boron-doped diamond electrodes: achieving 'fast mass transport' for 'slow diffusers'," *J. Electroanal. Chem.*, vol. 513, pp. 94-99, 2001.
- [3] K. Kobayashi, A. Chiba, and N. Minami, "Effects

of ultrasound on both electrolytic and electroless nickel depositions," *Ultrasonics*, 38, pp. 676-681 2000.

- [4] K. Kobayashi, A. Chiba, K. Tsuzuki, and N. Minami, "The Effects of ultrasound on faradaic processes and the interfaces of metal-electrolyte in copper electrodeposition systems," in *Proceedings of the 17<sup>th</sup> International Congress on Acoustics*, Rome, Italy, 2-7, September 2001, pp. 393-394.
- [5] J.O'M. Bockris and A.K.N. Reddy, *Modern Electrochemistry*, Plenum/Rosetta, New York, 1973.