



## Kinetic Electrode Reactions in Silver Electrodeposition Using a Multipulse Current Measurement

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The kinetics of electrode reactions in silver electrodeposition are investigated using a multipulse current measurement. The transient voltage drops across the anode and cathode electrodes in response to the applied multipulse currents are measured and analyzed with an analytical solution of unsteady-state equations comprising diffusion of ions, charge-transfer reactions, and a charging process of the electrochemical double layer. The measured voltage-time curves agree well with those predicted by the analytical solution. The kinetic constant, the exchange current density, and the double-layer capacitance, which characterize the kinetics of the electrode reactions, are determined.

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Manuscript submitted May 11, 2004; revised manuscript received July 27, 2004. Available electronically January 24, 2005.

Silver and silver alloy deposition in various electrolytes<sup>1-5</sup> have attracted scientific and technological interest. However, there have been very few reports on the kinetics of electrode reactions in silver electrodeposition. In particular, the kinetic constant, the exchange current density, and the double-layer capacitance in the ferrocyanide-thiocyanate electrolytes, which characterize the kinetics of the electrode reactions in silver electrodeposition, remain unknown.

We have proposed a multipulse current measurement<sup>6</sup> to investigate the kinetics of electrode reactions in nickel electrodeposition. The interesting point of the method is obtaining exponential-type curves related to a charging process of the double layer. In this paper, the method can also be applied to electrode reactions in silver electrodeposition, and the fundamental parameters described by the kinetic constant, the exchange current density, and the double-layer capacitance are presented.

In the multipulse current measurement, a small current density imposed between cathode and anode electrodes causes a concentration wave in the electrolyte near the cathode electrodes and a charging process of the electrochemical double layer. The transient behaviors of the voltage for the applied multipulse current can be measured within a time range of milliseconds. The concentration wave defined as a concentration of ions deviating from the thermal equilibrium is governed by Fick's diffusion equation, in which the wave is small enough to be treated as a perturbation. The governing equations, which are solved under a condition that the voltage between the electrodes is a few millivolts or less,<sup>7</sup> comprise the unsteady-state diffusion equation and an equivalent electric circuit. Fundamental parameters that describe the transient behaviors of the electrode reactions can be determined using the analytical solutions of the governing equations that represent the voltage response in the system to the square wave multipulse currents.

The purposes of this paper are to show that the measured voltage-time curves for silver electrodeposition are consistent with the analytical solution in more cases, to present the exponential-type curves related to the charging process of the double layer, and to determine the fundamental parameters such as the kinetic constant, the exchange current density, and the double-layer capacitance.

### Experimental

The ferrocyanide-thiocyanate electrolyte including the following components (g/L) was prepared: AgNO<sub>3</sub> 25.5 (99.8%); K<sub>4</sub>Fe(CN)<sub>6</sub> · 3H<sub>2</sub>O (99.5%), 72; KSCN (99.5%), 146; KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> · 4H<sub>2</sub>O (99.5%), 59.3; K<sub>2</sub>CO<sub>3</sub> (99.5%) 31.3. The numbers inside the parentheses are chemical purities. First, a mixed solution of AgNO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>4</sub>Fe(CN)<sub>6</sub> · 3H<sub>2</sub>O was boiled for 30 min and yielded burnt umber colored precipitates of iron hydroxides. After removal

of the iron hydroxide, the remaining components were added to the solution. The salt KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> acts as a supplementary stabilizer of antimony complex.

Polycrystalline copper plates 10 × 10 × 0.1 mm were prepared for the cathode electrodes. To avoid silver striking when the copper plate was immersed in the electrolyte, we electrodeposited silver on the copper plate in advance. The silver-electrodeposited surface seems to have a color of bright silver and a mirror-like appearance. A polycrystalline silver plate of 99.98 wt % purity was prepared for an anode electrode, of dimensions 60 × 60 × 1 mm. These electrodes, cleaned by a wet process, were located parallel in the quiescent electrolyte including the previously mentioned chemical compositions.

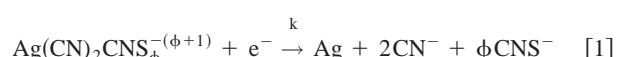
The two-electrode system is chosen because (i) the solution resistance in this system is negligibly small, (ii) the capacitance between the working and reference electrodes does not need to be taken into consideration, and (iii) the resistance and capacitance in series of the anode electrode can be ignored using an anode electrode with a large area. The area of the anode electrode was 36 times as large as that of the cathode electrode. Hence, we can neglect the resistance and capacitance in series of the anode electrode in the electrolyte compared with those of the silver-coated copper electrode.

Multipulse currents as shown in Fig. 1a were provided with a programmable bipolar power source through the electrochemical cell maintained at 300 K during electrodeposition. The cell voltage across the electrochemical cell was measured with a digital oscilloscope that allows us to record transient voltage-time curves. Silver electrodeposits were grown on the silver-coated copper substrates for the on-time time ranging from 4 to 8 ms.

### Results and Discussion

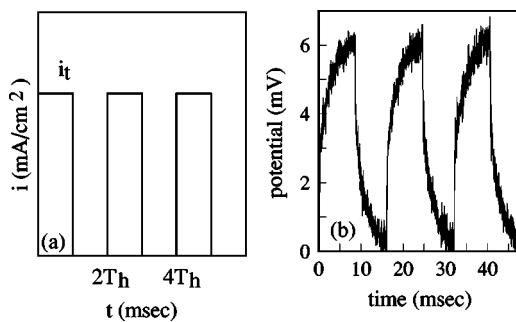
*Response of electrode reactions to multipulse currents.*—We have already reported in detail the analysis of transient voltage-time curves using multipulse current measurements.<sup>6</sup> We describe the method briefly.

The electrochemical reaction in silver electrodeposition<sup>5</sup> is considered to be



where  $\phi$  has a value within the range 1-2. The concentration of the silver complexant near the cathode electrode changes with a small multipulse current. The concentration change, which is described by the transient diffusion equation and boundary condition in one dimension, is given by

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**Figure 1.** Response of voltage to applied multicurrent steps. (a) Schematic illustration of multipulse current with current on-time  $T_h$  equal to current off-time. (b) Typical voltage-time curve for  $i_t = 0.8 \text{ mA/cm}^2$  and  $T_h = 8 \text{ msec}$ .

$$\frac{\partial \Delta c}{\partial t} = D \frac{\partial^2 \Delta c}{\partial x^2} \quad [2]$$

$$k(c^* - \Delta c) = -D \frac{\partial \Delta c}{\partial x}, \quad \text{at } x = 0$$

where  $\Delta c$  is a small concentration change of the silver complexant from the thermal equilibrium concentration  $c^*$  and  $D$  is the diffusion coefficient. Equation 2 can be solved under the boundary condition using a Laplace transformation such as  $\int_0^\infty e^{-pt} \Delta c dt$ . The solution of Eq. 2 at  $x = 0$  in Laplace space is

$$\Delta \bar{c}|_{x=0} = \frac{k c^*}{p(\sqrt{pD} + k)} \quad [3]$$

where  $\Delta \bar{c}$  indicates the concentration in Laplace space. For  $\Delta c/c^* \ll 1$ , the diffusion voltage  $\eta_d$  due to the deviation of the concentration at the thermal equilibrium<sup>7</sup> is linearized as

$$\eta_d = \nu \frac{RT}{nF} \ln \frac{c^* + \Delta c}{c^*} \approx \frac{\nu RT \Delta c}{nFc^*} \quad [4]$$

where  $\nu$  is the stoichiometric factor. The faradaic current density related to the charge-transfer reaction at the cathode electrode is

$$i_f = i_o \left[ \frac{c_O}{c_O^0} \exp\left(-\frac{\alpha z F \eta_c}{RT}\right) - \frac{c_R}{c_R^0} \exp\left(-\frac{(1-\alpha)z F \eta_c}{RT}\right) \right] \approx -\frac{i_o n F \eta_c}{RT} \quad [5]$$

where  $\alpha$  is the transfer coefficient for the process,  $c_O$  and  $c_R$  are the concentrations of the silver complexant and Ag,  $c_O^0$  and  $c_R^0$  are the thermal equilibrium concentrations of the silver complexant and Ag, respectively,  $i_o$  is the exchange current density, and  $\eta_c$  is the electrode voltage that occurs during the charge-transfer reaction. Here, we assume  $c_O = c_R$  and  $c_O^0 = c_R^0$ , as is often used in the analysis of electrode reactions,<sup>7,8</sup> and Eq. 4 and 5 are linearized under a reasonable approximation of  $\eta_c$  and  $\eta_d$  not exceeding a few millivolts. The voltage between the working and counter electrodes should be chosen to fulfill the condition that the measured voltages are less than a few millivolts.

Thus, the voltage of the double-layer capacitance  $\eta$ , which is equal to the sum of the electrode potential  $\eta_c$  and the diffusion potential  $\eta_d$ , can be related to the capacitance current density  $i_c$  according to the well-known equation

$$i_c = C \frac{d\eta}{dt} \quad [6]$$

where  $C$  is the electrochemical double-layer capacitance.

Next, let us consider a square wave current pulse at a time  $t$  where  $2mT_h < t < (2m+1)T_h$ , where  $T_h$  is the on-time and  $m$  is an integer. The square wave current step  $i$  applied between the cathode and anode electrodes at the time  $2mT_h < t < (2m+1)T_h$  is given by

$$i = i_t[u(t) - u(t - T_h) + u(t - 2T_h) - \dots - u(t - (2m+1)T_h)] \quad [7]$$

where  $u(t)$  is a step function and  $i_t$  is the peak current density, as shown in Fig. 1. The current on-time is here set equal to the current off-time. Equation 7 is also transformed into Laplace space

$$\bar{i} = \frac{i_t}{p} \frac{1 - e^{-2(m+1)pT_h}}{1 + e^{-pT_h}} \quad [8]$$

where  $\bar{i}$  indicates the current transformed into Laplace space. Thus, the current  $i$  through the electrochemical cell can be divided into two elements, the faradaic current density  $i_f$  and the capacity current density  $i_c$  that passes through the electrochemical double layer

$$i = i_c - i_f \quad [9]$$

Substituting Eq. 5 and 6 into Eq. 9, and again substituting Eq. 3 and 4 into the result, we have a mathematical form in Laplace space

$$\bar{\eta} = \frac{\bar{i}}{Cp + \frac{nFi_o}{RT}} + \frac{1}{Cp + \frac{nFi_o}{RT}} \cdot \frac{i_o k \nu}{p(\sqrt{pD} + k)} \quad [10]$$

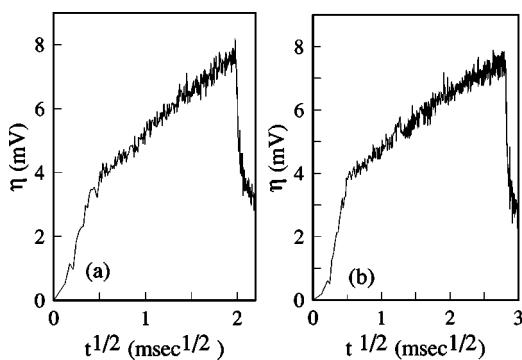
To obtain a solution in real space, the inverse Laplace transform<sup>9</sup> is applied to Eq. 10. The solution of the voltage-time function in real space becomes

$$\begin{aligned} \eta = & \frac{RTi_t}{nFi_o} \left( 1 - \frac{e^{-nFi_o T_h / CRT} - e^{-2mnFi_o T_h / CRT}}{1 + e^{-nFi_o T_h / CRT}} e^{-nFi_o t / CRT} \right) \\ & + \frac{2RTk}{nF\sqrt{D}} \sqrt{t} - \frac{RTk^2 \nu}{nFD} \int_0^t e^{k^2/D\theta} \operatorname{erfc} \left( k \sqrt{\frac{\theta}{D}} \right) d\theta \\ & - \frac{RTk\nu}{nF\sqrt{D}} \int_0^t e^{-nFi_o / CRT(t-\theta)} \frac{d\theta}{\sqrt{\pi\theta}} \\ & + \frac{RTk^2 \nu}{nFD} \int_0^t e^{-nFi_o / CRT(t-\theta)} e^{k^2/D\theta} \operatorname{erfc} \left( k \sqrt{\frac{\theta}{D}} \right) d\theta \quad [11] \end{aligned}$$

where  $\operatorname{erfc}(\cdot)$  is the complementary error function and the transformation  $t - 2mT_h \rightarrow t$  is used. For  $t \ll 1$ , the sum of the third and the fifth terms on the right-hand side in Eq. 11 tends to zero. The fourth term on the right-hand side in Eq. 11 can also be ignored because  $\exp(-nFi_o t / CRT) \ll 1$  for typical values of  $t \approx 10^{-3} \text{ s}$ ,  $RT/nF \approx 25.7 \times 10^{-3} \text{ V}$ ,  $i_o \approx 1 \times 10^{-3} \text{ mA/cm}^2$ , and  $C \approx 1 \mu\text{F}$  at room temperature. Consequently, for  $mT_h > 10^2$ , Eq. 11 is reduced

$$\eta = \frac{RTi_t}{Fi_o} (1 - e^{-nFi_o t / CRT}) + \frac{2RTk}{nF\sqrt{\pi D}} \sqrt{t} \quad [12]$$

Equation 12 explains well the physical responses of ions to the applied pulse current. The exponential term on the right-hand side in



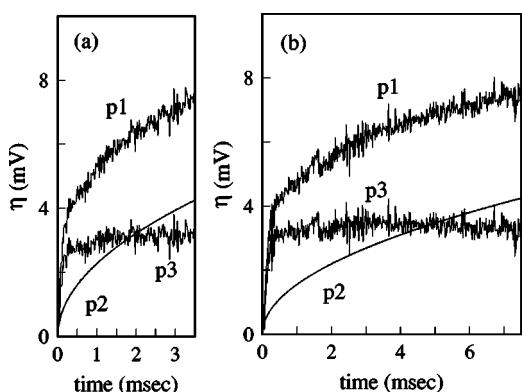
**Figure 2.** Plots of voltage  $\eta$  vs.  $t^{1/2}$  for (a)  $T_h = 4$  ms and (b)  $T_h = 8$  ms. The slope of the straight line is equal to  $2RTk/nF\sqrt{\pi D}$  in Eq. 12.

Eq. 12 is related to a charging process of the electrochemical double layer. The square root of time represents the movements of the ions by diffusion.

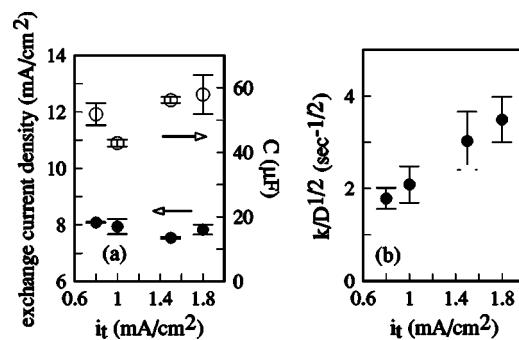
This report will show that Eq. 12 is true not only for the single crystalline electrode used in the previous paper<sup>6</sup> but also for the polycrystalline electrodes. This method can be applied to more cases. In addition, the necessary condition of  $\exp(-nFi_0t/CRT) \ll 1$  for Eq. 12 proves right in more cases.

*Applications of Eq. 12 to the voltage-time curves.*—A typical plot of the transient voltage drop for the applied multipulse current densities is shown in Fig. 1. For the on-time  $T_h$  of 8 ms at a current density of  $0.8 \text{ mA/cm}^2$ , the voltage drop between the electrodes increases with time and lags the current. This means that the current through the double-layer capacitor leads the voltage across the double-layer capacitor. Each voltage-time curve has the same response to the current pulse, which indicates that  $2mT_h$  is so large that the exponential term including  $2mT_h$  in Eq. 11 can be ignored.

We show how to derive the fundamental parameters describing the kinetic electrode reactions from the measured voltage-time curves. According to Eq. 12, as time proceeds,  $\eta$  should be proportional to the square root of time. Figure 2 shows a plot of  $\eta$  vs.  $t^{1/2}$  for  $T_h = 4$  and 8 ms. The slopes best fitted to the data in Fig. 2a and b are  $2RTk/nF\sqrt{\pi D}$  in Eq. 12. In Fig. 3, subtracting the calculated curve p2 from the measured voltage-time curve p1, we have an exponential-type curve p3 that corresponds to the second term on the right-hand side in Eq. 12. Figure 3 shows that the measured



**Figure 3.** Plots of measured voltage-time curves p1, the calculated  $t^{1/2}$ -type curves p2, and the exponential-type curves p3 obtained from p1-p2: (a)  $T_h = 4$  ms, (b)  $T_h = 8$  ms. (a) and (b) correspond to Fig. 2 a and b, respectively.



**Figure 4.** Fundamental parameters in electrode reactions. (a) Plot of exchange current density  $i_o$  vs.  $i_t$  for  $T_h = 8$  ms and plot of double-layer capacitance  $C$  vs.  $i_t$  for  $T_h = 8$  ms. (b) Plot of  $k/D^{1/2}$  vs.  $i_t$  for  $T_h = 8$  ms.

voltage-time curves for  $T_h = 4$  and 8 ms are divided into two curves. The two curves p3 in Fig. 3 appear to be an exponential-type function that has a saturated value. Thus, the voltage-time function represented by Eq. 12 is justified. The three constants in Eq. 12,  $RTi_t/Fi_o$ ,  $nFi_o/CRT$ , and  $2RTk/nF\sqrt{\pi D}$ , can be determined from the results in Fig. 2 and 3.

Figure 4a is a plot of the exchange current density  $i_o$  vs.  $i_t$ , which is obtained from the values of  $RTi_t/Fi_o$ . The exchange current density is almost independent of the applied current density. The average exchange current density for this study is  $7.8 \pm 0.2 \text{ mA/cm}^2$ . Figure 4a also shows a plot of the double-layer capacitance  $C$  vs.  $i_t$ , which is determined from the values of  $nFi_o/CRT$ . The double-layer capacitance is almost independent of  $i_t$ . The average double-layer capacitance is estimated at  $52.1 \pm 6.5 \mu\text{Fcm}^{-2}$ . Figure 4b shows that  $k/\sqrt{D}$  is linearly proportional to  $i_t$ . The exchange current of  $2.4 \text{ mA/cm}^2$  and the double-layer capacitance of  $90-160 \mu\text{Fcm}^{-2}$  are reported in silver electrodeposition in cyanide electrolyte<sup>10</sup> using electrochemical impedance spectroscopy. These values, which result using a cyanide electrolyte different from our electrolyte, are not far from the experimental values in this study.

## Conclusions

The measured voltage-time curves agree well with the analytical solutions for the three transient processes comprising the diffusion of ions in electrolyte, charge-transfer reactions, and a charging process of the electrochemical double layer. The proposed method can be applied to more cases. The kinetic constant, the exchange current density, and the double-layer capacitance characterizing the kinetics of the charge-transfer reactions are determined from the measured voltage-time curves using the proposed analytical solution.

## Acknowledgment

The author thanks Hideki Higa of the University of the Ryukyus for the experimental preparations.

*The University of the Ryukyus assisted in meeting the publication costs of this article.*

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