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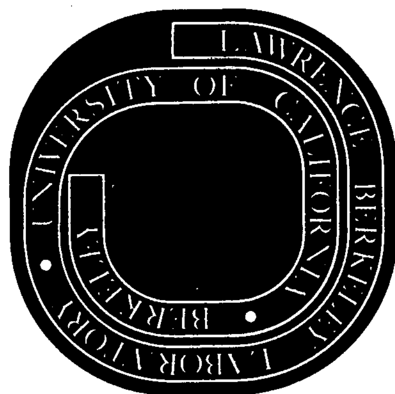

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INTERPRETATION OF THE IMPEDANCE PROPERTIES OF THE ANODE-SURFACE FILM IN THE ELECTROPOLISHING OF COPPER IN PHOSPHORIC ACID

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August 1972

ABSTRACT

The frequency dispersion of the impedance measured by Ohashi, et al., between a vertical copper anode and a reference electrode during electropolishing in concentrated phosphoric acid is analyzed in terms of linear combinations of resistors and capacitors.

The frequency dependence of the anode under electropolishing conditions may be satisfactorily represented by an analogue circuit consisting of a resistor and a capacitor connected in parallel. The resistivity is in the range of 4.5-5 ohm·cm^2 while the capacitance is 5-8 μF/cm^2. The contribution of the solution-side resistance to the total impedance is small. Assuming that the solid film layers on the anode surface are composed of oxides of copper, depending on actual composition, the measured impedances are consistent with a thickness range of 13-124 Angstroms.

Key words: Anodic films, Electropolishing, Impedance of surface films, Anodic dissolution of copper in phosphoric acid.

INTRODUCTION

The question of the presence of an invisible anode solid film during copper electropolishing in concentrated phosphoric acid has been a subject of investigation by many researchers in recent years. The mercury test by Hoar and his coworkers (1,2) and an ellipsometric study of the anode in situ by Novak, et al., (3) provide strong evidence of the existence of a solid film on the surface.

Electrical properties of the anode-electrolyte interface during electropolishing have been explored by Ohashi, Murakawa and Nagaura(4) by means of AC impedance measurements. A reinterpretation of these experimental impedance data allow inferences about the nature of the invisible solid film.

IMPEDANCE OF THE ANODE FILM IN THE ELECTROPOLISHING REGION*

The A. C. impedance between a vertical anode and a reference electrode during electropolishing was measured by Ohashi, et al., (4) in the frequency range of 400 hertz to 10 KHz. They have interpreted their experimental results in terms of a resistor, R_s, and a capacitor, C_s, connected in series. The series resistance R_s decreases sharply while C_s decreases only slightly with increase of frequency. However, for this analogue to represent the experimental impedance values, both the series resistance, R_s, and capacitance, C_s must be independent of

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*Section of current plateau below the onset of transpassive region.

0 0 0 0 3 8 0 0 4 7 9

frequency. Obviously, the series connection of a resistor and a capacitor doesn't represent the measured impedance properly.

The wave length range of A. C. used by Ohashi, et al. (400 Hz to 10 KHz) is many orders of magnitude larger than the dimensions of the anode specimen. This allows an equivalent circuit to be represented by linear elements. We exclude here nonlinearity caused by roughness of the surface on the microscale. One of the equivalent circuits to be considered for non-porous films of uniform properties along the anode surface is shown in Fig. 1. It is assumed that there is no special adsorption of ions affecting the anode impedance. The Warburg impedance is probably negligible in the high frequency range.

Assuming that either the solid side or the solution side is the controlling factor of the over-all anode impedance, one greatly simplified equivalent circuit is the parallel connection of a resistor and a capacitor with series resistors as shown in Fig. 2.

The total impedance across points A and R, Z_{ar}, for the equivalent circuit shown in Fig. 2 is given by:

$$Z_{ar} = \frac{R_x}{1 + \omega^2 R_x^2 C_x^2} + R_{ar} + R_{sc} - j \frac{\omega R_x^2 C_x}{1 + \omega^2 R_x^2 C_x^2} \qquad (1)$$

in which ω is the angular frequency. For the series connection of a resistor and a capacitor, used by Ohashi, the following relation holds:

$$Z_{ar} = R_s - j \frac{1}{\omega C_s} \qquad (2)$$

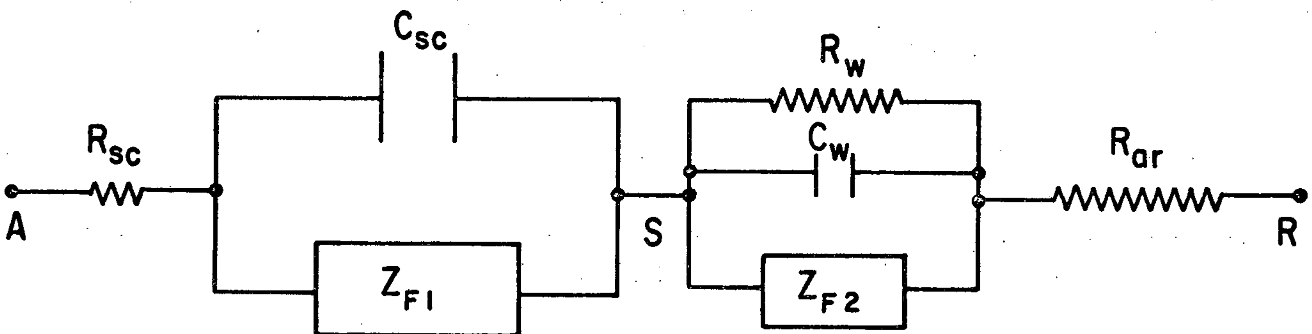

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Fig. 1. Analogue circuit representing the electrical characteristics of the copper/solid film/solution system.

R_{sc}: series resistance of the solid film
C_{sc}: capacitance of the solid barrier layer
R_w: double layer resistance
C_w: double layer capacitance
R_{ar}: resistance due to the electrolyte between the anode and reference electrode
Z_{F1}: Faradaic impedance on the solid side
Z_{F2}: Faradaic impedance on the solution side
Point A: copper
Point S: solid film/solution interface
Point R: reference electrode

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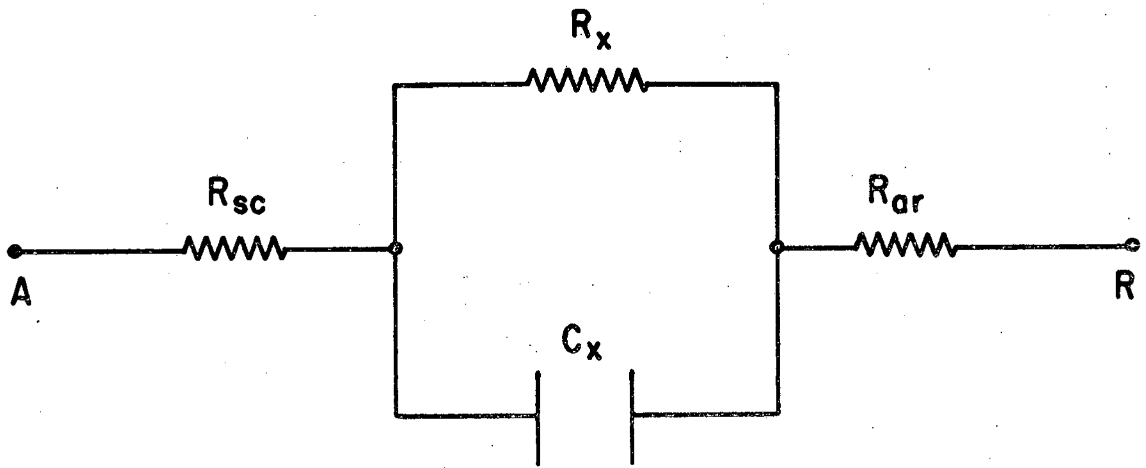


Fig. 2. Simplified analogue circuit.

Comparing Eq. (1) with Eq. (2), we get

$$R_s = R_{ar} + R_{sc} + \frac{R_x}{1 + \omega^2 R_x^2 C_x^2} \tag{3}$$

and

$$\frac{1}{\omega C_s} = \frac{\omega R_x^2 C_x}{1 + \omega^2 R_x^2 C_x^2} \tag{4}$$

From these equations we obtain (5)

$$\left(\frac{R_x}{1 + \omega^2 R_x^2 C_x^2} - \frac{R_x}{2}\right)^2 + \left(\frac{\omega R_x^2 C_x}{1 + \omega^2 R_x^2 C_x^2}\right)^2 = \left(\frac{R_x}{2}\right)^2 \tag{5}$$

or

$$\left(R_s - R_{ar} - R_{sc} - \frac{R_x}{2}\right)^2 + \left(\frac{1}{\omega C_s}\right)^2 = \left(\frac{R_x}{2}\right)^2 \tag{6}$$

Equation (6) is the equation of a circle which is centered at $(R_x/2,0)$ with radius $R_x/2$, if the measured reactance, $1/\omega C_s$, is plotted against resistance, $R_s - R_{ar} - R_{sc}$. The values of R_{ar} and R_{sc} have been estimated in two ways: (1) from extrapolating the measured values of R_s vs. 1/f (Ref. 4) to infinite frequency, and (2) from the measured values of the resistance between the anode and the reference electrode when the anode dissolves in the active region.

Figure 3 shows the impedance loci of the Cu/solid film/soln./reference electrode system, when the anode potential is 1.0 V < E_n < 1.3 V and the frequency is in the range of 400 Hz to 10 KHz. The experimental data points fall close to a circle of 16 Ω diameter. This suggests that the analogue circuit of a parallel resistor and a parallel capacitor is approximately correct. In Figs. 4 and 5, the parallel resistance $R_{x,o}$ (Ωcm^2) and parallel capacitance $C_{x,o}$ ($\mu F/cm^2$) of the analogue circuit per unit area of the apparent surface are plotted as functions of frequency. $R_{x,o}$ is nearly independent of frequency, although it slightly decreases with the increase of anode potential. Figure 5 shows that $5\ \mu F/cm^2 < C_{x,o} < 8\ \mu F/cm^2$.

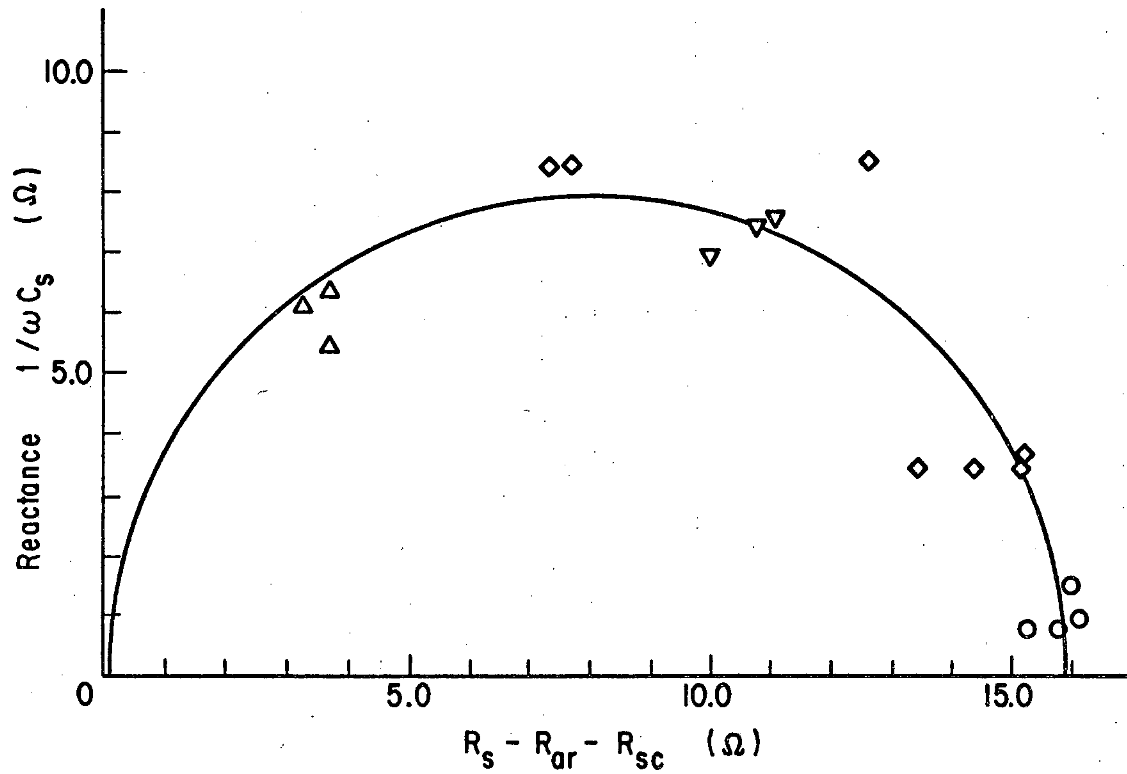
The foregoing analysis indicates that the impedance of the anode surface under electropolishing conditions can be satisfactorily represented by the parallel connection of a resistor and a capacitor, instead of the series combination suggested by Ohashi, et al. (4).

Effect of Solution-Side Impedance

We shall now examine whether the impedances, R_x and C_x, are predominantly determined by the solution side impedance, R_w, C_w and Z_{F2}. The fact that $R_{x,o}$ and $C_{x,o}$ are nearly independent of frequency suggests that under Ohashi's experimental conditions the effect of the diffusion impedance on the over-all impedance is small.

Assuming the diffusion impedance to be negligible, we get

$$\frac{1}{R_x} \simeq \frac{1}{R_w} + \frac{1}{R_T} \tag{7}$$



$1.0\ V < E_h < 1.3\ V$

○ 400 Hz ▽ 3 KHz

◇ 1 KHz △ 10 KHz

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Fig. 3. Impedance loci of the copper/solid film/solution/reference electrode system (calculated by equation 6). $1.0\ V < E_h < 1.3\ V$. Data by Ohashi, et al. (4).

0 0 3 0 3 8 0 0 4 8 2

and

$$C_x \simeq C_w \qquad (8)$$

The reaction resistance R_T may be calculated by the following relation (6)

$$R_T = \left(\frac{\partial E_h}{\partial i}\right)_{i=i_l} \simeq \frac{RT}{\alpha_a F i_l} \qquad (9)$$

in which the Tafel relation $(i = i_o \exp(\alpha_a \eta_a F/RT))$ is assumed to be applicable. If we assume that for the anodic transfer coefficient, α_a, in Eq. (9) we can use the value obtained for the active dissolution of copper (α_a = 1.44 (7)), we obtain for i_l = 0.018 A/cm^2* at 30°C:

$$R_T \simeq 1\ \Omega cm^2 \quad .$$

This leads to $R_{x,o} < 1\ \Omega cm^2$. As shown in Fig. 6, in the electropolishing region the observed $R_{x,o}$ is of the order of 4.5 - 5.0 Ωcm^2. $R_{x,o}$ in the active dissolution of copper is probably much smaller than that in the electropolishing region (Fig. 6). Considering R_T to be the slope of the anodic polarization curve at a given current density, it is evident under electropolishing conditions the observed $R_{x,o}$ doesn't represent the solution-side resistance.

We now turn our attention to the behavior of capacitance. From Ohashi's experimental data the parallel capacitance, $C_{x,o}$, in active

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*The current density used in Ohashi et al.'s experiments (4).

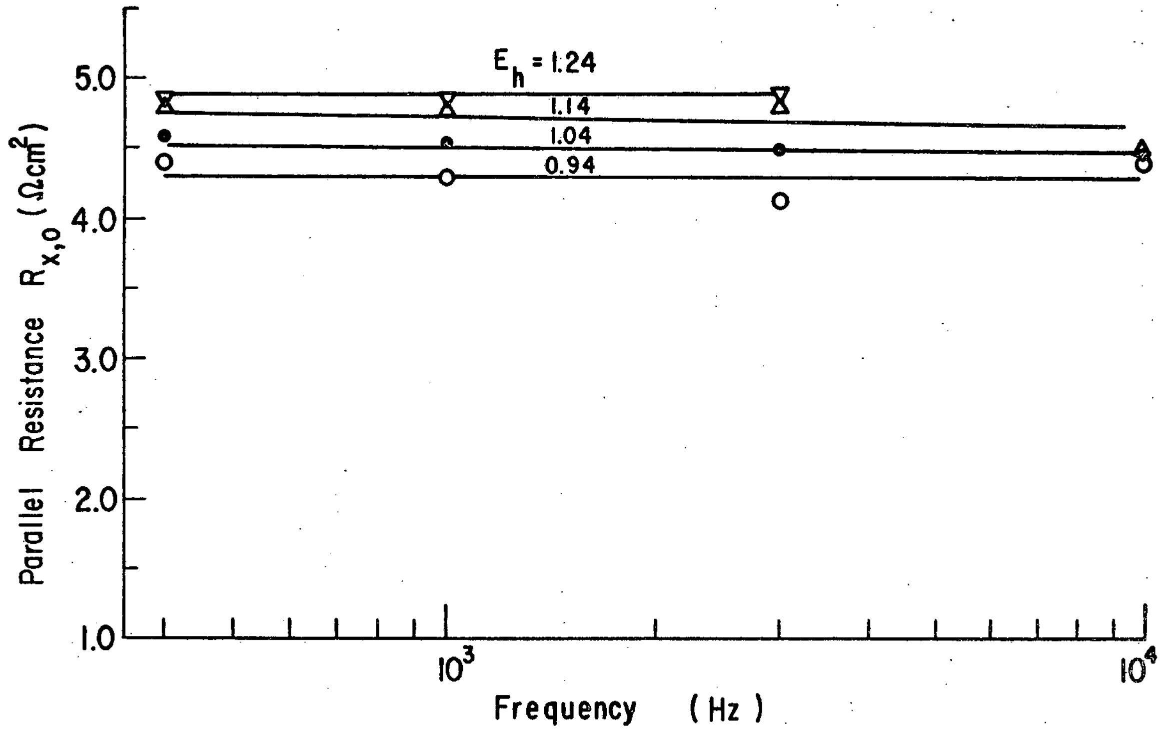

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Fig. 4. Effect of frequency on the parallel resistance $R_{x,o}$ (this work). Data by Ohashi et al. (4).

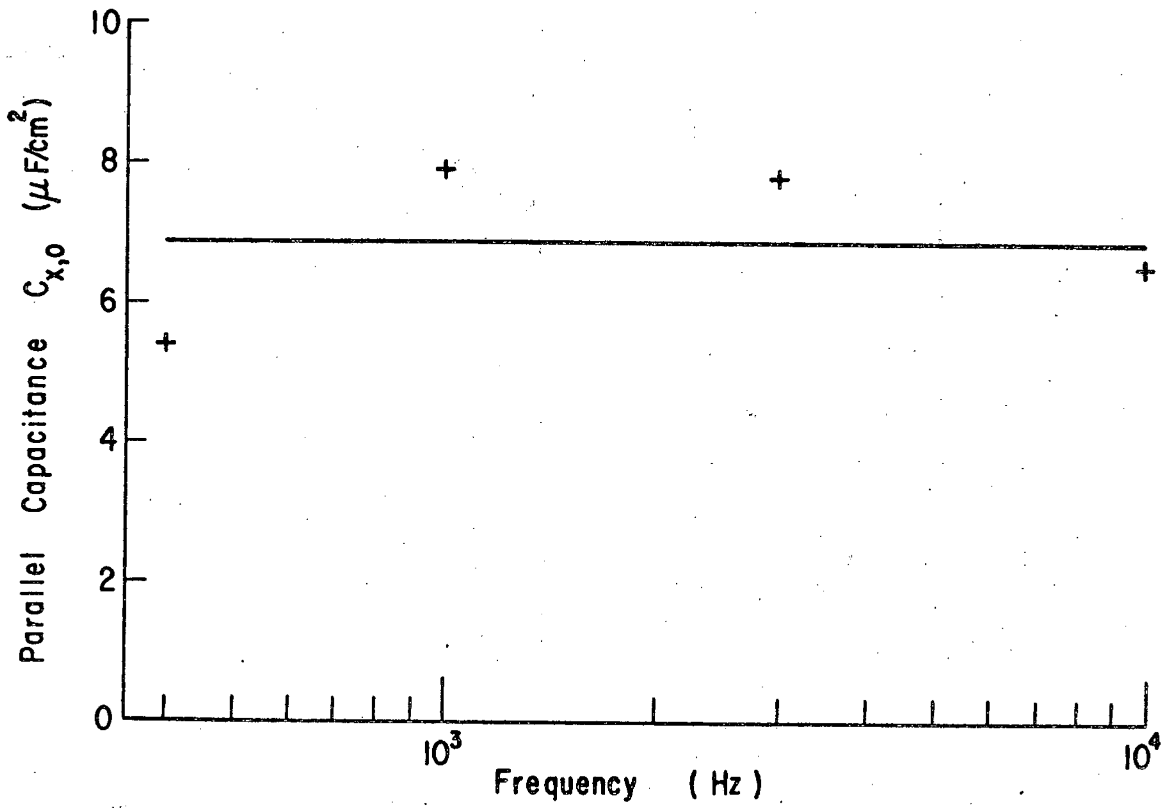

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Fig. 5. Effect of frequency on the parallel capacitance $C_{x,o}$
E_h = 1.04 - 1.24 V (this work).

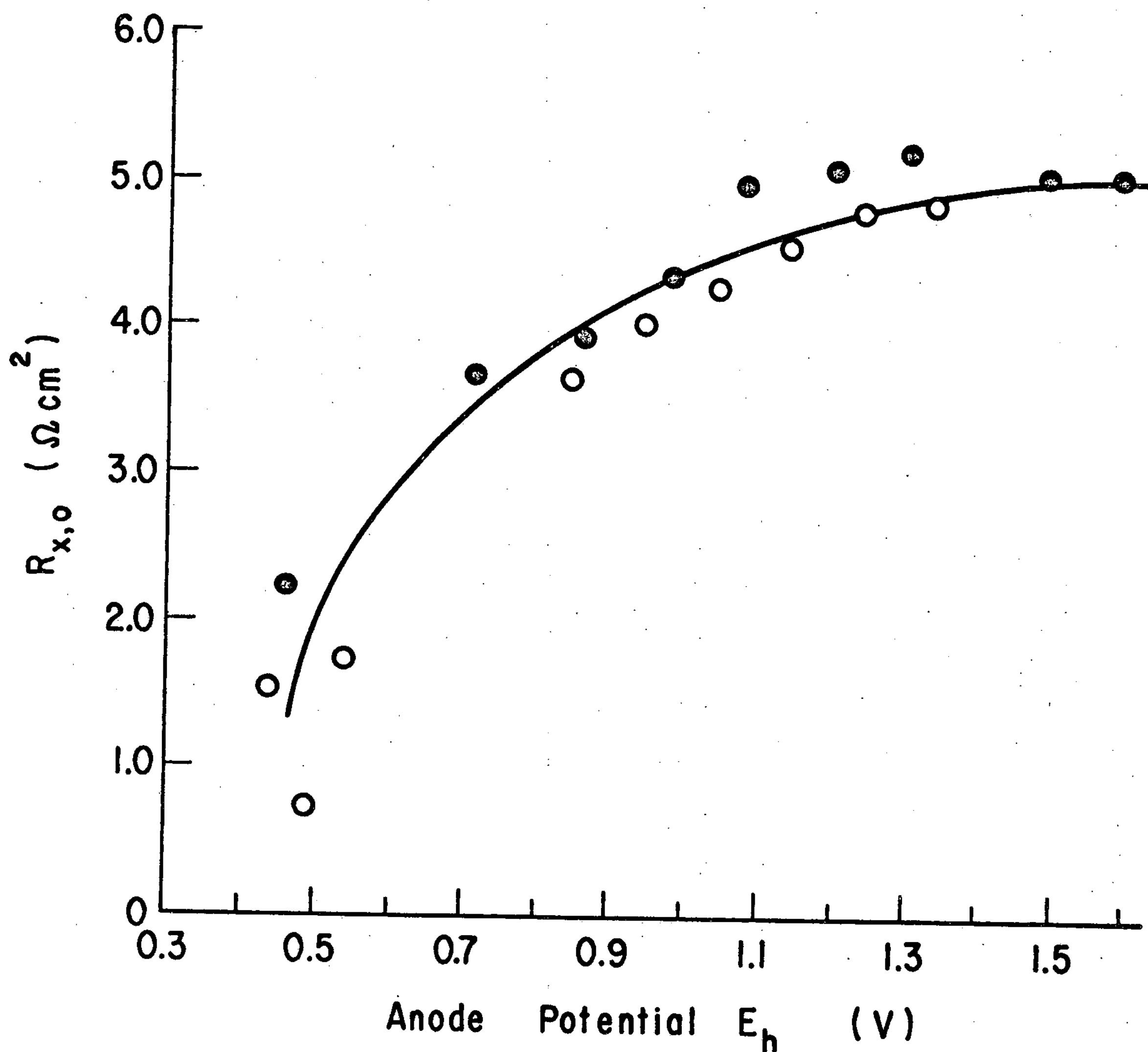

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Fig. 6. Effect of anode potential on the parallel resistance $R_{x,o}$ at f = 1 KHz (this work). Data by Ohashi, et al. (4). Best electropolishing region: $1.0 < E_h < 1.6$ V. Active dissolution occurs when $E_h < 0.4$ V (7).

dissolution of copper is of the order of 200 - 800 μF/cm^2. According to Bockris and Conway (8), Hoey (9), Noguet (10), et al., at $E_h > 0.3$ V** the double-layer capacitance of copper electrodes is of the order of 100 μF/cm^2 or higher. Even after a correction for surface roughness is made, the double-layer capacitance is still too large compared to the values of $C_{x,o}$ under electropolishing conditions.

It is concluded that the parallel resistance and capacitance obtained under the conditions of electropolishing don't represent the impedance at the anode/solution interface. This is in agreement with the results obtained with respect to the electrode reactions at the current plateau (1,7). It should be mentioned that according to Hoey (9) the effect of the solution-side impedance on the over-all impedance of the Cu/Cu_2O/aqueous solution system may be neglected when no direct current passes, and the frequency is larger than 10^3 Hz.

SOLID FILM PROPERTIES

We now examine the second extreme case, in which the impedance of the solid film is represented by parallel resistor and capacitor (R_x, C_x). The order of magnitude of the solid film thickness θ_f, then, may be estimated by

$$\theta_f \simeq \frac{\varepsilon_o \varepsilon_f f}{C_{x,o}} = 8.854 \times 10^{-14} \frac{\varepsilon_f}{C_{x,o}} f \qquad (10)$$

in which ε_f and f are the dielectric constant of the solid film and the roughness factor of the film, respectively. A study of the rest potential

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**Anode potential region in which active dissolution of copper occurs.

of copper anodes at the current plateau (7,11), as well as electron diffraction studies (12,13,14,15,16,17) of electropolished copper indicate that the anode during electropolishing is covered with copper oxides. According to Noguet, et al., (10) and Heltemes (17) the dielectric constant of Cu_2O is 7.5 - 7.6, while that of CuO is 18 (Ref. 18). On the other hand, Hoey (9) has found that a film of the multi-layer structure composed of Cu_2O, CuO, and an unidentified higher copper oxide has a dielectric constant of the order of 46 - 70, much higher than that of pure Cu_2O or CuO (7). Assuming that the possible range of the dielectric constant of the anode solid film is 7.5 - 70 and that for well electropolished surfaces the roughness factor f is 1.3 (19), we obtain from Eq. (10).

$$\theta_f \simeq 13 - 124 \text{ Å}$$

If any portion of the solid film functions as a series resistor, the film thickness should be larger than 13 - 124 Å.

According to Hoar (20) the film thickness estimated from impedance data is of the order of 6 to 60 Å. Using an ellipsometric technique, Novak, et al., (3) have found recently that the film thickness is of the order of 40 to 120 Å at a limiting current density close to that in Ohashi's impedance experiments.

If the film thickness is really of the order of magnitude mentioned above, copper ions will transfer through the solid film under the electric field of 10^6 - 10^7 V/cm. Under this high field, the current

density passing through an anode film is approximately given by the following form (21,22)

$$i = A_2 \exp (B E) \tag{11}$$

in which the apparent field strength, E, is given by $E = \Delta\eta_f/\theta_f$, where $\Delta\eta_f$ is the apparent overvoltage at the anode. The value of B may be estimated from the relation

$$R_{x,o} = \left(\frac{\partial E_h}{\partial i}\right)_{i_l} = \frac{\theta_f}{i_l B} \tag{12}$$

Equation (12) yields $B = (1.5 - 14) \times 10^{-6}$ cm/V for $\theta_f = 13 - 124$ Å and $i = 0.018$ A/cm^2. It is interesting to note that the value of B is 6.8×10^{-6} cm/V for a 60 Å film, which is proposed to be the probable value of the film thickness by Novak, et al. The fact that the value of B for a 60 Å film is of the same order of magnitude as that for anodic oxide films formed on Ta, Al, Zr, Nb, InSb, etc. (22) under a high electric field strength gives strong support to the view that copper ions transfer through the anode film under the high electric field. For this reason, $R_{x,o}$ should be interpreted as the over-all reaction resistance of the solid film.

Finally, it is necessary to consider to what degree our interpretation of impedance measurements may be affected by nonisothermal conditions. When large current densities pass through the resistive film, the rate of heat generation by the Joule effect may be considerable. A

temperature rise of the film may cause flow of electrolyte near the anode, causing a non-uniform current-density distribution. Assuming that in Ohashi's experiments the heat generated in the solid film was transferred to the electrolyte primarily by natural convention, we can estimate the order of magnitude of the average film temperature, T_e, at steady state:

$$T_e - T_{soln} \approx \frac{0.24\ i_l^2}{h_m} \left(R_{x,o} - \frac{\Delta\eta_f}{i_l} \right) \tag{13}$$

in which T_{soln}, i_l, and h_m are the temperature of the electrolyte in immediate contact with the anode, the limiting current density, and heat-transfer coefficient, respectively. The heat-transfer coefficient has been estimated (7) using the well established correlation between Nu and Gr·Pr for heated vertical plates (23). Nu, Gr, and Pr are Nusselt number, Grashof number, and Prandtl number respectively. For the thermal conductivity and the thermal coefficient of volumetric expansion, the respective physical properties of water have been used. The calculated temperature difference, $(T_e - T_{soln})_{calc.}$ is of the order of 1°C or smaller. Since in fact heat is also lost by thermal conduction through the back of the anode the temperature difference, $T_e - T_{soln}$, is probably smaller than 1°C.

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CONCLUDING REMARKS

The impedance of the anode under electropolishing conditions may be approximately represented by the parallel connection of a resistor and a capacitor. The resistance of the parallel resistor starts to increase in the anode-potential region in which the passivation of copper by cuprous oxide takes place (7). The parallel resistance is nearly constant in the electropolishing potential region. Lowering of limiting current in the electropolishing region shows that the parallel resistance affects the over-all transport resistance of copper ions.

The generally accepted exponential form for ion transport under high field may be applicable for the transport of copper ions through the solid film.

ACKNOWLEDGMENT

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