

# Power-Law Behavior of Reaction Impedance in Titanium Anodizing

M. Saitou\*, M. Mori and S. Kawamoto

Department of Mechanical Systems Engineering, University of the Ryukyus, 1 Senbaru Nishihara-cho Okinawa, 903-0213, Japan

**Abstract:** We have investigated the dependence of reaction impedance in titanium anodizing on the frequency of a small sine wave voltage superimposed on a fixed D.C. voltage. The magnitude of the reaction impedance,  $|Z|$  is found to obey a power law of the angular frequency  $\omega$ ,  $|Z| \propto \omega^{-\alpha}$ . The exponent  $\alpha$  of  $0.52 \pm 0.05$ , which was determined by the measurement of the frequency-dependent  $|Z|$ , indicates that in the titanium anodizing process, a homogeneous charge-transfer reaction takes place in the interfacial layer between the anode electrode and the outer Helmholtz plane.

**Keywords:** power-law, homogeneous charge-transfer reaction, reaction impedance, titanium, anodizing.

## 1. INTRODUCTION

Titanium anodizing has been studied in the fields of nanoscience [1], medical engineering [2] and electrochemistry [3] because of scientific interests and practical applications. Two different interpretations of the titanium anodizing process have been proposed. One interpretation is described by the electrochemical reaction [2, 4, 5] such as  $Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$ , which can be read as a heterogeneous charge-transfer reaction in which both reactants exist in the different two phases. That is, in the charge-transfer reaction a titanium atom in titanium anode electrode and water molecules adsorbed on the titanium anode electrode react electrochemically.

The other interpretation [1, 3, 6] states that titanium atoms dissolve into an electrolyte and anodic oxidation takes place at the interface. The electrochemical reaction that occurs in a diffusion layer of titanium ions is called a homogeneous charge-transfer reaction given by  $Ti^{4+} + 2H_2O \rightarrow TiO_2 + 4H^+$ .

The same discrepancy as seen in titanium anodizing has been reported in the study on the aluminum anodizing process [7,8], which is described as  $2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$  for the heterogeneous charge-transfer reaction and  $2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+$  for the homogeneous charge-transfer reaction.

Studies on the charge-transfer reaction contribute to the understanding of the interface between an electrode and electrolyte in many fields [9-11]. However, there have been very few studies that combine the charge-transfer reaction with a power law.

The magnitude of the reaction impedance,  $|Z|$  due to a change in a reactant concentration caused in the vicinity of

an anode electrode by a small sine wave voltage with an angular frequency  $\omega$  [12] obeys the power law,

$$|Z| \propto \omega^{-\alpha}, \quad (1)$$

where the exponent  $\alpha$  has a value of 0.5 for the homogeneous charge-transfer reaction and that of 1.0 for the heterogeneous charge-transfer reaction. We have developed a measurement method [13] for the reaction impedance in electrodeposition, which is based on a perturbation theory that describes the small change in the reactant concentration caused by the applied small voltage.

The present paper aims at showing that the reaction impedance in titanium anodizing obeys the power law and the homogeneous charge-transfer reaction takes place.

## 2. EXPERIMENTAL SETUP

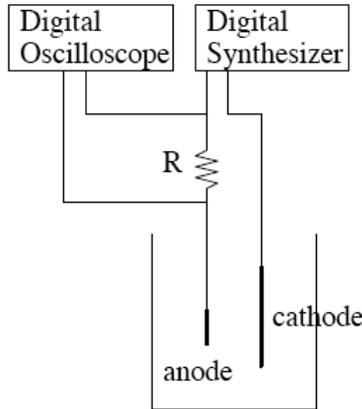
A square titanium plate (the Nilaco corp.) of 7 mm in width and 1 mm in thickness and a titanium sheet (the Nilaco corp.) of 65mm in length, 60 mm in width, and 1 mm in thickness were used for the anode and cathode electrode. The electrodes were made of titanium of 99.5 wt % purity. The anode electrode polished by the use of 5, 1 and 0.1 $\mu$ m diamond powder pastes appeared to be mirror-like. The cathode electrode was also polished with a 1200 SiC grit paper. The resistance and capacitance ( for example, the capacitance of the double layer ) in series with the cathode electrode in the electrolyte can be neglected in comparison with those of the anode electrode because the area of the cathode electrode was about 80 times as large as that of the anode electrode.

An ultrasonic cleaner with the distilled water, acetone, and ethanol in order was used for 10 minutes to clean the electrode. The anode and cathode electrode were located parallel in a cell including a solution of 1 mol/L phosphoric acid (Kanto chemical Co. Inc.). The electrochemical cell was maintained at a temperature range of 292 to 302 K.

A small sine wave voltage having an amplitude of 10 - 90 mV and a frequency of 1 - 25 Hz, which was superimposed on a DC voltage (NF corp., WF1965), was applied between the anode and cathode electrode. As shown in Fig. (1), the

\*Address correspondence to this author at the Department of Mechanical Systems Engineering, University of the Ryukyus, 1 Senbaru Nishihara-cho Okinawa, 903-0213, Japan; E-mail: saitou@tec.u-ryukyuu.ac.jp

resistance  $R$  of  $50 \Omega$  was connected in the system to measure a current passing between the anode and cathode electrode and the data of the current was stored in a digital oscilloscope (Yokogawa, DL1720). The AC coupling mode in the digital oscilloscope operation was chosen to measure only the A. C. component of the current.



**Fig. (1).** Schematic diagram for measurements of transient potential curves for a sine wave voltage generated by the digital synthesizer.

In our preliminary experiment, for a D. C. voltage of 4 V, the current density rapidly decreased at the initial stage and at an anodizing time of 100 s the transient current gradually tended to be a fixed current density of  $2.6 \text{ mA/cm}^2$ . This indicated that the anodizing rate at 100 s was very low but no corrosion of the formed titanium layer occurred because the corrosion current for the anodized titanium [14] was an order of  $\mu\text{A/cm}^2$ . Thus, the D.C. voltage on which the small sine wave voltage was superimposed was determined as 4 V.

### 3. RESULTS AND DISCUSSION

#### 3.1. Power-Law of Reaction Impedance

The small sine wave voltage causes a change in a reactant concentration in the vicinity of the anode electrode surface. The concentration change behaves as if electrical components in the equivalent circuit model, and fluctuates with a phase shift electrically observed as impedance called the reaction impedance.

The governing equations for the homogeneous and heterogeneous charge-transfer reaction become  $\partial\Delta c/\partial t = D\nabla^2\Delta c - k\Delta c$  and  $\partial\Delta c/\partial t = \nu i/nF - k\Delta c$  where  $t$  is the time and  $\Delta c$  is defined by a small change of the ion concentration from the thermal equilibrium concentration,  $D$  is the diffusion coefficient,  $k$  is the net rate related to electron charge transfer reactions,  $i$  is the current density,  $n$  is the charge number,  $F$  is the Faraday constant and  $\nu$  is the stoichiometric factor.

As we have reported in detail how to solve the equation under some appropriate boundary conditions [13], we here briefly describe the results. For the homogeneous charge-transfer reaction, the magnitude of the reaction impedance  $|Z|$  becomes,

$$|Z| = \left( \frac{RT\nu^2}{n^2 F^2 \bar{c} \sqrt{D}} \right) \left( \frac{1}{\omega^2 + k^2} \right)^{1/4}, \quad (2)$$

where  $R$  is the gas constant,  $\omega$  is the angular frequency of the sine wave voltage and  $T$  is the temperature. It is noted that Eq. (2) indicates not the impedance without reaction (called the Warburg impedance) but the impedance with reaction. Eq. (2) represents the impedance when the charge-transfer reaction takes place in the electrolyte and titanium ions bind chemically to oxygen ions in the electrolyte. On the other hand, for the heterogeneous charge-transfer reaction, the magnitude of the reaction impedance becomes,

$$|Z| = \left( \frac{\nu^2 RT}{n^2 F^2 \bar{c}_s} \right) \frac{1}{\sqrt{\omega^2 + k^2}}, \quad (3)$$

where  $\bar{c}_s$  is the equilibrium concentration at the surface. It is noted that Eq. (3) includes no diffusion coefficient. We assume that in this study the net reaction rate constant  $k$  is  $k < 1$  [15]. For  $\omega > k$ , Eqs. (2) and (3) are summarized as Eq. (1).

The other electrical components in the equivalent circuit model are the capacitance of the anodized titanium oxide layer and that of the Helmholtz layer. These capacitances connected in series with the reaction impedance can be neglected because they are in general much larger [16-18] than the reaction capacitance. Hence, the measured impedance becomes the reaction impedance.

#### 3.2. Reaction Impedance for the Small Sine Voltage Superimposed on the DC Voltage

To extract the amplitude of the current density caused by the small sine wave voltage superimposed on the D.C. voltage, the Fourier transform [19] is employed. Here let us consider the Fourier transformation of the cosine wave current density,  $i$  with a pulse time duration of  $p$ , which is defined by,

$$\begin{aligned} i_0 \cos \omega_0 t, & \quad \text{for } 0 \leq t \leq p, \\ 0, & \quad \text{for } t < 0 \text{ and } t > p, \end{aligned} \quad (4)$$

where  $i_0$  is the amplitude of the cosine wave current density and  $\omega_0$  is the angular frequency of the applied sine wave voltage. The data of the cosine wave current density within the interval  $[0, p]$  are transformed into Fourier space, that is, Eq. (4) is transformed into Fourier space,

$$\begin{aligned} F(\omega) &= pi_0/2, \quad \text{for } \omega = \omega_0, \\ F(\omega) &= \frac{\sin p(\omega - \omega_0)/2}{\omega - \omega_0} + \frac{\sin p(\omega + \omega_0)/2}{\omega + \omega_0}, \quad \text{for } \omega \neq \omega_0. \end{aligned} \quad (5)$$

Eq. (5) shows that the magnitude of the reaction impedance  $|Z|$  is determined by  $F(\omega)$  using the known sine wave voltage and the value of  $p$ . For the sine wave voltage superimposed on a D. C. voltage of 4 V, the measured current density in Fig. (2a) is transformed into Fourier space in Fig. (2b). The applied sine wave voltage has amplitude of 40 mV and a frequency of 1 Hz. According to Eq. (5), the intense peak of  $|F(\omega)|$  appears at 1 Hz as shown in Fig. (2b).

In a similar way, for the sine wave voltage having an amplitude from 10 to 90 mV and a frequency from 1 to 25 Hz,  $|F(\omega)|$ , which is linearly proportional to the amplitude of the sine wave voltage, is obtained as shown in Fig. (3). As stated in the Introduction, Eqs. (2) and (3) are derived on the

basis of the linear perturbation theory that requires the Ohm's law to define the reaction impedance. The experimental results in Fig. (3) satisfy the required condition of linearity between the applied sine wave voltage and the current density. Fig. (3) gives the reciprocal value of  $|Z|$  from  $p=100$  and the slope in a plot of  $|F(\omega)|$  vs the amplitude of the applied sine wave voltage.

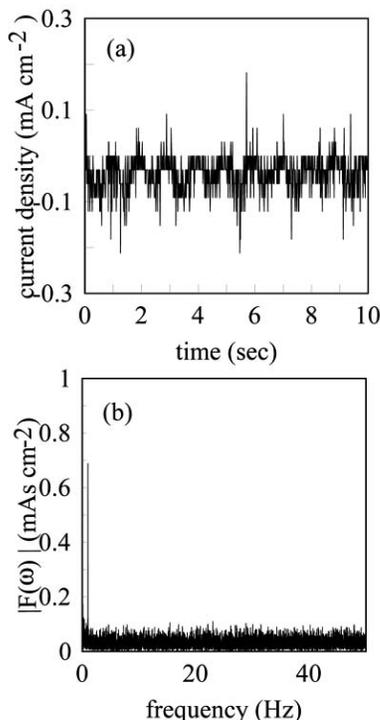


Fig. (2). Typical current density vs time curve at 292 K using the 1 mol/L phosphoric acid solution and its Fourier transformation plot. (a) Current-time curve obtained for the 1 Hz sine wave voltage having an amplitude of 40 mV superimposed on the DC 4 V. The DC component in the current is excluded. (b) Fourier transformation of the data in (a). The intense peak is obtained at 1 Hz.

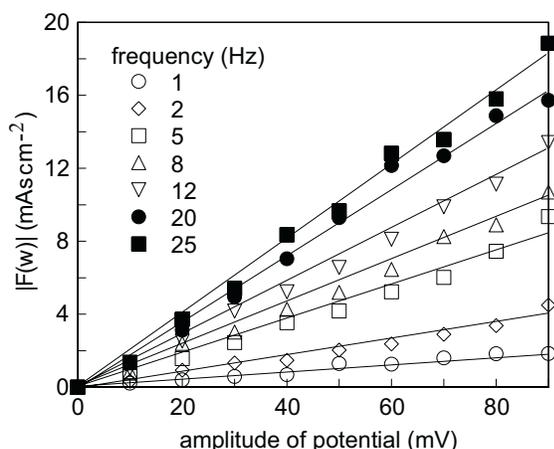


Fig. (3). Dependence of the amplitude of the current density in Fourier space on the amplitude of the sine wave voltage at 292 K.

In Fig. (4),  $|Z|$  is shown to obey the power law of the angular frequency,  $|Z| \propto \omega^{-\alpha}$ . The exponent value of  $\alpha$  best fitted to the data,  $0.48 \pm 0.04$  at a temperature of 292 K indicates that in titanium anodizing, the homogeneous charge transfer reaction occurs. In addition, irrespective of temperature, as shown in Fig. (5), the reaction impedance obeys the power law and the slope best fitted to all the data yields the exponent  $\alpha$  of  $0.52 \pm 0.03$ . In addition, the impedance decreases with temperature. Hence, in titanium anodizing, the homogeneous charge-transfer reaction takes place in the electrolyte between the electrode surface and the outer Helmholtz layer. As a thin titanium oxide layer have a porous structure [20], titanium atoms in contact with the phosphoric acid solution dissolve and electrochemically react to the oxygen ions, which is described by  $Ti^{4+} + 2H_2O \rightarrow TiO_2 + 4H^+$ . In our experiment, as the film thickness is estimated at about 20 nm, the homogeneous charge transfer reaction becomes the mechanism for the oxide layer.

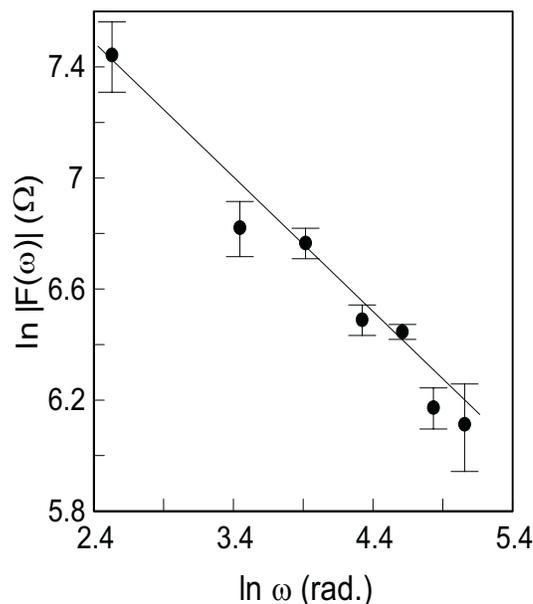
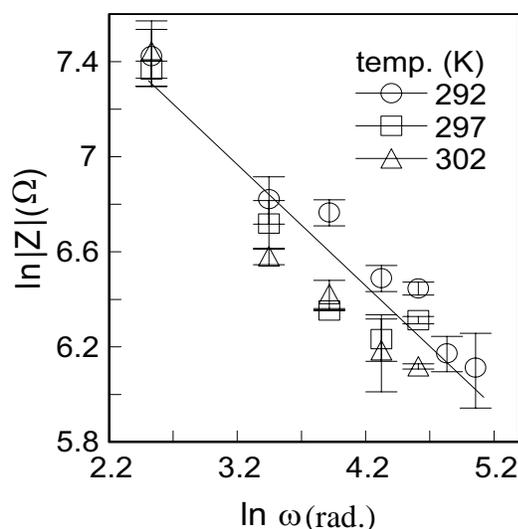


Fig. (4). Log-log plot of the reaction impedance vs the angular frequency at 292 K. The DC voltage and the amplitude of the sine wave voltage are 4 V and 40 mV.

In potentiostatic oxidizing, no pH change in the phosphoric acid solution affects the growth rate and growth thickness of the titanium oxide layer [20]. However, the pH affect the dissolution and corrosion behaviors of titanium oxide layers potentiostatically formed [3, 4]. Hence, the power-law behavior of the formed oxide layer in a corrosion circumstance will need a further study.

#### 4. CONCLUSIONS

We have investigated the type of the charge-transfer reactions in titanium anodizing. It is shown that the reaction impedance obeys the power law,  $|Z| \propto \omega^{-\alpha}$ , and that the



**Fig. (5).** Log-log plot of the reaction impedance vs the angular frequency for three kinds of the electrolyte temperature. The straight line best fitted to the data is shown.

exponent  $\alpha = 0.52 \pm 0.03$  for the anodizing process is obtained. This indicates that in the titanium anodizing process the charge-transfer reaction takes place at the interface, at which both titanium ion and water molecule exist.

#### REFERENCES

- [1] Yang XY, Huang QY. Application of organic electrolytes in  $\text{TiO}_2$  nanotubes fabrication. *Prog Chem* 2009; 21: 116-20.
- [2] Diamanti MV, Pedferri MP. Effect of anodic oxidation parameters on the titanium oxides formation. *Corrosion Sci* 2007; 49: 939-48.
- [3] Frayret C, Botella P, Jaszay T, Delville MH. Titanium dissolution-passivation in highly chloridic and oxygenated aqueous solutions. *J Electrochem Soc* 2004; 151: B543-50.
- [4] Schultze JW, Lohrengel MM. Stability, reactivity and breakdown of passive films. *Electrochim Acta* 2000; 45: 2499-513.
- [5] Marino CE, de Oliveira EM, Rocha RC, Biaggio SR. On the stability of thin-oxide films of titanium in acid phosphoric media. *Corrosion Sci* 2001; 43: 1465-76.
- [6] Jaszay T, Caprani A, Priem F, Frayret JP. On the anodic dissolution of titanium between 15 °C and 100 °C in deaerated 2 M hydrochloric acid. *Electrochim Acta* 1988; 33: 1093-100.
- [7] Thompson GE. Porous anodic alumina. *Thin Solid Films* 1997; 297: 192-201.
- [8] Wood GC, Skeldon P, Thompson GE, Shimizu K. A model for the incorporation of electrolyte species into anodic alumina. *J Electrochem Soc* 1996; 143: 74-83.
- [9] Tapsoba I, Haouas B, Boujlel K. Oxidation by heterogeneous and homogeneous electron transfer of N-amidoimidates. *J Electroanal Chem* 2004; 574: 107-12.
- [10] Michman M. Homogeneous vs heterogeneous processes in electrocatalysis. *J Mol Catal* 1996; 107: 393-8.
- [11] David IG, Diaconu M, Radu GL, David V. Investigation of the some electron transfer bioprocess by voltammetric techniques. *Roum Biotechnol Lett* 2002; 7: 603-24.
- [12] Vetter KJ. *Electrochemical kinetics*. New York: Academic Press 1967.
- [13] Saitou M, Hashiguchi R. Kinetics of electrode reaction on (110) single-crystalline nickel electrode in nickel sulfamate using a multipulse current measurement. *J Phys Chem B* 2003; 107: 9404-8.
- [14] Lohrengel MM. Pulse measurements for the investigations of fast electronic and ionic processes at the electrode/electrolyte interface. *Ber Bunsenges Phys Chem* 1993; 97: 440-7.
- [15] Hwang BJ, Hwang JR. Kinetic model of anodic oxidation of titanium in sulphuric acid. *J Appl Electrochem* 1993; 23: 1056-62.
- [16] Marsch J, Gorse D. A photoelectrochemical and ac impedance study of anodic titanium oxide films. *Electrochim Acta* 1997; 43: 659-70.
- [17] Lohrengel MM. Thin anodic oxide layers on aluminium and other valve metals. *Mater Sci Eng* 1993; R11: 243-94.
- [18] Dey A, De S, De A, De SK. Characterization and dielectric properties of polyaniline- $\text{TiO}_2$  nanocomposites. *Nanotechnology* 2004; 15: 1277-83.
- [19] Hwei PH. *Fourier analysis*, New York: Simon & Schuster, Inc. 1970.
- [20] Delplancke JL, Winand R. Galvanostatic anodization of titanium. *Electrochim Acta* 1988; 33: 1539-49.

Received: May 29, 2009

Revised: June 15, 2009

Accepted: June 19, 2009

© Saitou *et al.*; Licensee Bentham Open.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.