



A.c. Impedance Measurement of CP-Ti in 0.1 M NaOH Solution

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ABSTRACT :

A.c. impedances of mechanically polished CP-Ti specimens were measured at open-circuit potential (OCP) with immersion time and under applied anodic potentials between -0.2 and 1 $V_{Ag/AgCl}$ in 0.1 M NaOH solution. Capacitances of native oxide films ($C_{ox,na}$) grown naturally and capacitances of anodic oxide films ($C_{ox,an}$) formed under applied anodic potentials were obtained to examine the growth of native and anodic oxide films in 0.1 M NaOH solution and how to use $C_{ox,na}$ for the surface area measurement of Ti specimen. $1/C_{ox,na}$ and $1/C_{ox,an}$ appeared to be linearly proportional to OCP and applied potential (E_{app}), with proportional constants of 0.086 and 0.051 $\mu F^{-1} V^{-1}$, respectively. The $C_{ox,na}$ also appeared to be linearly proportional to geometric surface area of the mechanically polished CP-Ti fixture specimen, with proportional constants of 11.3 and 8.5 $\mu F cm^{-2}$ at -0.45 $V_{Ag/AgCl}$ and -0.25 $V_{Ag/AgCl}$ of OCPs, respectively, in 0.1 M NaOH solution. This linear relationship between $C_{ox,na}$ and surface area is suggested to be applicable for the measurement of real surface area of Ti specimen.

Keywords : A.c. impedance, Titanium, Capacitance, Oxide film, Surface area measurement

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1. Introduction

Titanium and its alloys have been used for dental implants because of their excellent biocompatibilities, good mechanical properties, low density and excellent corrosion resistance. The excellent biocompatibilities of Ti are attributed to its ability to form native oxide film on the surface spontaneously.¹⁻³⁾ The native oxide film also provides excellent corrosion resistance because it is highly stable in corrosive medium. The surface oxide films on Ti can be thickened by the application of anodic potentials which render better biocompatibilities and corrosion protection.^{1,4-9)}

Growth behavior of anodic oxide films on Ti has been investigated largely in acid⁴⁻⁹⁾ and alkaline solutions.^{9,10)} The growth of the anodic oxide film on Ti in acids was investigated by E-t curves, cyclic voltam-

metry,¹¹⁾ ellipsometry,¹²⁾ and a.c. impedance method.^{11,13-19)} The anodic oxide film on Ti is well known to form barrier type or porous type in acid or in high alkaline solutions. The electronic properties of the oxide dielectric and semiconductive properties were investigated using electrochemical impedance spectroscopy.¹³⁻¹⁹⁾ Although many works have been carried out on the anodic oxide formation on Ti, most of them were focused on the electrical or corrosion properties of oxide films in acidic solutions and there is still lack of information on the anodic oxide growth on Ti in alkaline solution, and the information on the oxide film capacitance for the mechanically polished Ti surface with different areas has not been reported.

In this work, a.c. impedance measurement was performed on the mechanically polished CP-Ti specimens at open-circuit potential (OCP) and under applied anodic potentials in 0.1 M NaOH solution, and capacitances of native oxide films ($C_{ox,na}$) and anodic oxide films ($C_{ox,an}$) were obtained to clarify the growth of

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native and anodic oxide films and to examine how to use $C_{ox,na}$ for the surface area measurement of Ti specimen.

2. Experimental

CP-Ti (grade 4) of Ti fixture specimens without external screws at the outer surface presented by Fig. 1 were employed for the a.c. impedance measurement in this study. Apparent surface areas of the fixture specimens are 0.97, 1.19, 1.43 and 1.66 cm². An inner screw at one end of the fixture specimen was machined which was used for pressing against PEEK mechanically to expose external surface area only and for connecting electrically. The fixture specimen was polished using 1 μ m alumina powder with ethanol, cleaned ultrasonically for 10 min in acetone, and then used for the a.c. impedance measurement.

A.c. impedance measurements were performed on the mechanically polished Ti fixture specimens in 0.1 M NaOH solution at 20°C using a Solartron 1255B FRA with a SI1287 electrochemical interface. The impedance was measured at open-circuit potential (OCP) with immersion time and under applied anodic potentials (E_{app}) from -0.2 to 1 V_{Ag/AgCl} by superimposing an a.c. signal of 5 mV_{rms} amplitude in the frequency range between 10 kHz to 1 Hz. The impedance was measured using a three electrode system with a platinum counter electrode and Ag/AgCl reference electrode. The impedance measurement under E_{app} was performed after application of E_{app} for 10 min when the potential was stepped up but it was measured directly after the application of E_{app} when it was stepped down. The impedance data were analyzed using ZVIEW2 equivalent circuit fitting/simulation program based on the complex non-linear least square



Fig. 1. Ti fixture specimens used for the measurement of a.c. impedance.

(CNLS) method.

3. Results and Discussion

Fig. 2 shows experimental (symbols) and fitted a.c. impedance spectra (line) for the mechanically polished Ti fixture specimen in 0.1 M NaOH solution at 20°C. The impedance data show a capacitive arc with high real and imaginary impedances more than kilo ohms at 1 Hz. The measured impedance data were analyzed by fitting using an equivalent electric circuit in Fig. 3. The equivalent circuit consists of the oxide film resistance R_{ox} connected in parallel to constant phase element which is related with the capacitance of oxide films C_{ox} . Fitting error of C_{ox} calculated by the ZVIEW2 simulation program appeared to be less than

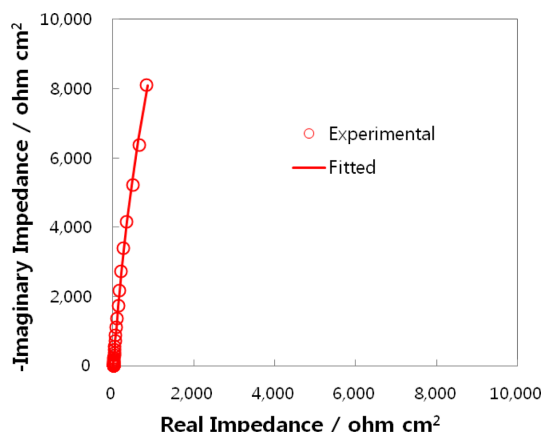


Fig. 2. Typical Nyquist plots obtained from the Ti fixture specimen with immersion time in 0.1 M NaOH solution at 20°C.

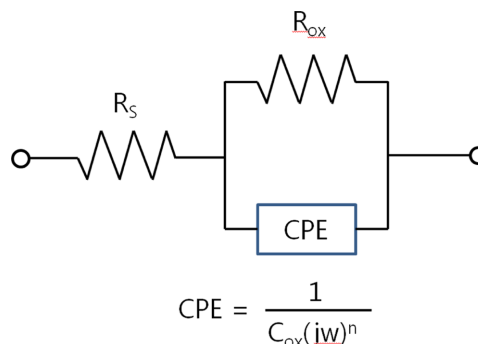


Fig. 3. An equivalent electric circuit used for fitting of a.c. impedance data. CPE = constant phase element, C_{ox} = oxide film resistance, n = depression parameter.

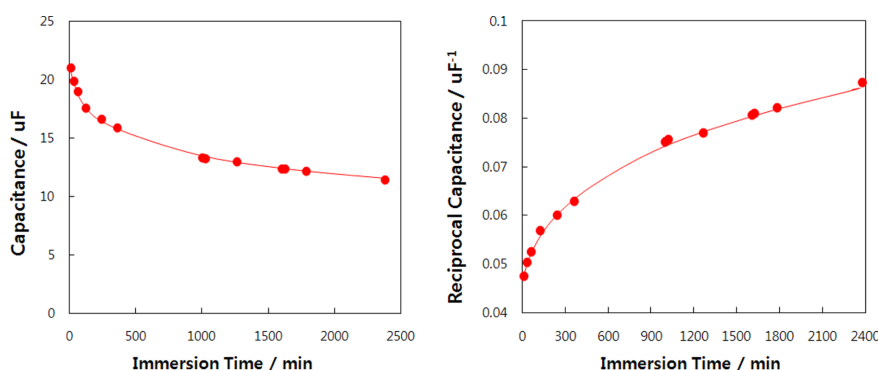


Fig. 4. Capacitance (a) and reciprocal capacitance (b) of native oxide film grown on the Ti fixture specimen measured at open-circuit potential with immersion time in 0.1 M NaOH solution at 20°C.

0.6%, which indicates that the data adjusted well to the proposed equivalent circuit. The depression parameter n value in CPE was obtained between 0.96–0.97, close to 1, representing that the surface of the Ti specimen acts like an ideal capacitor. It is readily inferred that the high impedances results from native oxide films with high ionic and electronic resistances on the Ti surface.

The capacitance and reciprocal capacitance values are demonstrated with immersion time in Fig. 4. The oxide capacitance decreased rapidly in the initial stage of immersion and its decreasing rate decreased with immersion time, while the reciprocal capacitance showed fast increase in the initial stage of immersion and then its increasing rate became slower with immersion time in 0.1 M NaOH solution.

Fig. 5 presents open-circuit potential behavior of the

mechanically polished Ti fixture specimen with immersion time in 0.1 M NaOH solution. It is interesting to note that behavior of open-circuit potential (OCP) with immersion time is quite similar to that of the reciprocal capacitance in Fig. 5(b). In order to see the relationship between OCP and reciprocal capacitance, the reciprocal capacitance was plotted as a function of OCP in Fig. 6. It is clear that the reciprocal capacitance of native oxide films grown on the mechanically polished CP-Ti surface is linearly proportional to OCP in 0.1 M NaOH solution, with a proportional constant of $0.086 \text{ uF}^{-1} \text{ V}^{-1}$. Considering that anodic oxide film thickness is linearly proportional to reciprocal capacitance of anodic oxide film on Ti,^{14,17)} it can be suggested that the thickness of native oxide films is proportional to OCP when it is grown natu-

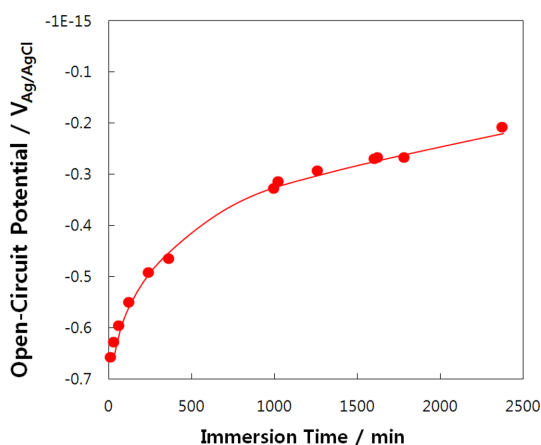


Fig. 5. OCP transient of the Ti fixture specimen in 0.1 M NaOH solution at 20°C

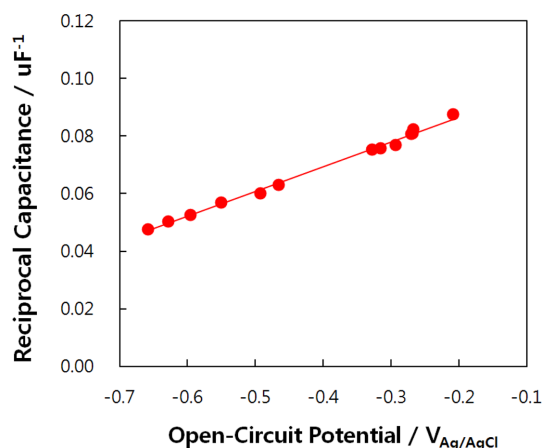


Fig. 6. Capacitance (a) and reciprocal capacitance (b) of the Ti fixture specimen with open-circuit potential in 0.1 M NaOH solution at 20°C.

rally with immersion time on the mechanically polished CP-Ti surface in 0.1 M NaOH solution. However, it should be also pointed out that if the Ti surface is covered with thick oxide films already, OCP could not represent the thickness of native oxide films on the Ti surface.

The oxide capacitance is generally written as

$$C_{ox} = \epsilon_0 \epsilon_{ox} A / l_{ox} \quad (1)$$

where ϵ_0 is the vacuum permittivity ($8.85 \times 10^{-12} \text{ F m}^{-1}$), ϵ_{ox} is the relative permittivity of the oxide films, A is the exposed area to the electrolyte and l_{ox} represents the oxide film thickness. If ϵ_{ox} and l_{ox} are constant, real surface area of the Ti surface can be obtained from the measured C_{ox} based upon the linear relationship between C_{ox} and A .

Fig. 7 illustrates the relationship between C_{ox} and geometric surface area of the mechanically polished CP-Ti fixture specimens measured at open-circuit potentials in 0.1 M NaOH solution. It is apparent that C_{ox} is proportional to the geometric surface area with slopes of 11.3 and $8.5 \mu\text{F cm}^{-2}$ at $-0.45 \text{ V}_{\text{Ag/AgCl}}$ and $-0.25 \text{ V}_{\text{Ag/AgCl}}$, respectively. Thus, it can be concluded that the surface area of mechanically polished CP-Ti specimen with alumina powder could be estimated by measuring the oxide capacitance based on the linear relationship in Fig. 7. It should be mentioned that the linear relationship between C_{ox} and surface area could be applicable for the surfaces finished by the same

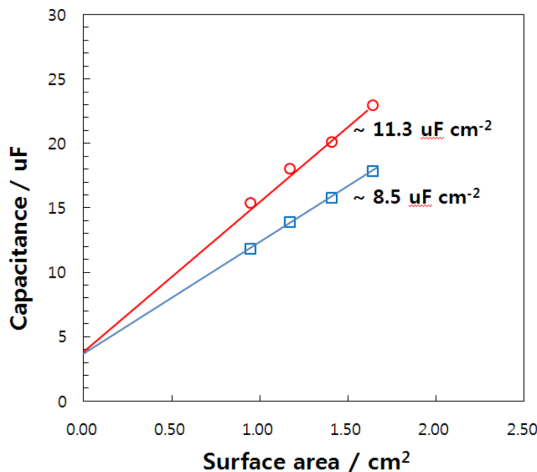


Fig. 7. Capacitance of native oxide films measured at various open-circuit potentials for the Ti fixture specimens with different apparent surface areas in 0.1 M NaOH solution at 20°C.

treatment conditions at the same open-circuit potential at which ϵ_{ox} and l_{ox} could be constant.

Fig. 8 depicts the changes in capacitance and reciprocal capacitance of anodic oxide films with applied anodic potential (E_{app}) on the mechanically polished CP-Ti fixture specimens, measured at constant anodic potentials stepped from -0.2 up to $1 \text{ V}_{\text{Ag/AgCl}}$ and then stepped down to $-0.2 \text{ V}_{\text{Ag/AgCl}}$ successively in 0.1 M NaOH solution. The anodic oxide film capacitance showed a large decrease with E_{app} when it was stepped up in the range between $-0.2 \text{ V}_{\text{Ag/AgCl}}$ to $1 \text{ V}_{\text{Ag/AgCl}}$ but it showed an almost constant value during potential drop from 1 to 0.8, 0.6 and then $0.4 \text{ V}_{\text{Ag/AgCl}}$, independent of applied potential. These mean that anodic films are grown under E_{app} up to $1 \text{ V}_{\text{Ag/AgCl}}$ and they are not dissolved significantly during potential drop in

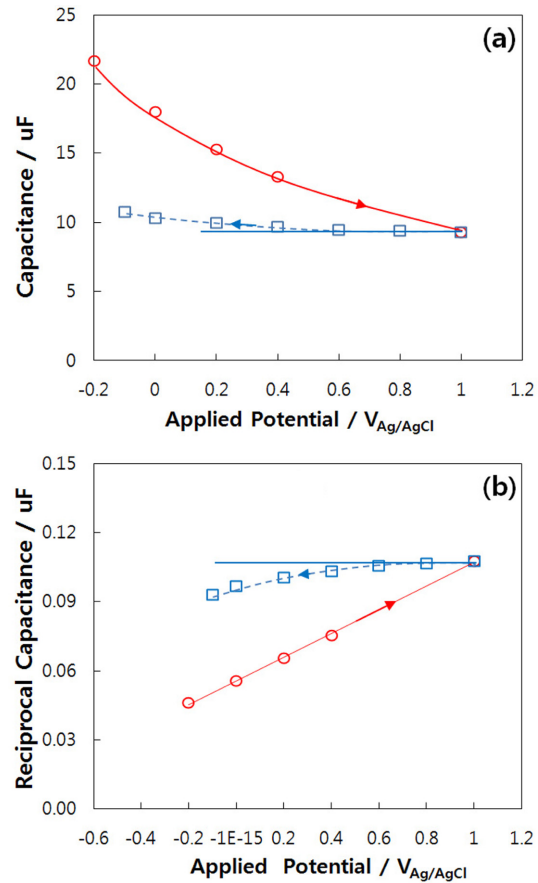


Fig. 8. Capacitance (a) and reciprocal capacitance (b) of the Ti fixture specimen at various applied anodic potentials during positive scan (circles) and negative scan (squares) in 0.1 M NaOH solution at 2°C.

0.1 M NaOH solution. $1/C_{\text{ox,an}}$ of the mechanically polished CP-Ti fixture specimen was obtained to be linearly proportional to E_{app} in 0.1 M NaOH solution, with a proportional constant of $0.051 \text{ uF}^{-1} \text{ V}^{-1}$, suggesting that anodic oxide film thickness increased linearly with applied potential as reported in the literature.⁶⁾

It is worth mentioning that the slope of $1/C_{\text{ox,an}}-E_{\text{app}}$ plot in Fig. 8(b) is lower than that of the $1/C_{\text{ox,na}}-\text{OCP}$ plot in Fig. 6, which seems to be related with differences in thickness and charge transfer reaction rates through the native and anodic oxide films at OCP and E_{app} . The difference in relative permittivity between the native and anodic oxide films would be influenced by the space charges in the films so it could be one of possible reasons for the different slopes between $1/C_{\text{ox,na}}-\text{OCP}$ plot and $1/C_{\text{ox,an}}-E_{\text{app}}$ plot. The measurement of surface area using EIS under the anodic potentials will be reported and discussed in view of the surface finishing conditions in the following paper.²⁰⁾

4. Conclusions

A.c. impedances of the mechanically polished CP-Ti fixture specimens were measured at open-circuit potential (OCP) with immersion time and under applied anodic potentials up to $1 \text{ V}_{\text{Ag/AgCl}}$ in 0.1 M NaOH solution. Capacitances of native oxide films ($C_{\text{ox,na}}$) grown naturally and capacitances of anodic oxide films ($C_{\text{ox,an}}$) formed under applied anodic potentials on the mechanically polished CP-Ti fixture specimen were precisely obtained with small error less than 0.6% by fitting the a.c. impedance data based on an electric equivalent circuit. The $C_{\text{ox,na}}$ of the mechanically polished CP-Ti fixture specimen decreased with immersion time, while its OCP increased with immersion time in 0.1 M NaOH solution. Reciprocal capacitance of the native oxide films ($1/C_{\text{ox,na}}$) showed similar behavior of OCP with immersion time in 0.1 M NaOH solution, and a linear relationship between them with a proportional constant of $0.086 \text{ uF}^{-1} \text{ V}^{-1}$ was found. Reciprocal capacitance of anodic oxide films ($1/C_{\text{ox,an}}$) formed on the mechanically polished CP-Ti fixture specimen up to $1 \text{ V}_{\text{Ag/AgCl}}$ showed also a linear increase with applied anodic potential in 0.1 M NaOH solution, with a proportional constant of $0.051 \text{ uF}^{-1} \text{ V}^{-1}$. The $C_{\text{ox,na}}$ appeared also to be linearly proportional to geometric surface area of the mechanically polished CP-Ti fixture specimen, with propor-

tional constants of 11.3 and 8.5 uF cm^{-2} at $-0.45 \text{ V}_{\text{Ag/AgCl}}$ and $-0.25 \text{ V}_{\text{Ag/AgCl}}$ of OCPs, respectively, in 0.1 M NaOH solution. The linear relationship between $C_{\text{ox,na}}$ and surface area could be used for the measurement of real surface area of Ti specimen.

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