Electrochemical Properties of Titanium in PEFC Bipolar Plate Environments

Yasutaka Soma*, Izumi Muto and Nobuyoshi Hara

Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

In order to assess the applicability of titanium as a bipolar plate for polymer electrolyte fuel cells (PEFCs), the electrochemical surface characteristics of commercially available pure titanium were examined in simulated PEFC conditions. The results of the electrochemical tests showed that the cathode operating potential of PEFC, 0.64 V (vs. Ag/AgCl(3.33 kmol-m⁻³ KCl)), lay in the anodic passivation region for titanium. The operating potential of the PEFC anode, –0.36 V, lay in the cathodic region or the cathodic to anodic transition region. Under the PEFC cathode condition, a barrier-type film with high charge transfer resistance and high contact resistance formed on the specimen. Under the PEFC anode condition, an oxide film with low charge transfer resistance and low contact resistance formed by a dissolution-precipitation mechanism.

1. Introduction

Recent research has brought various types of fuel cells closer to practical application. In particular, the polymer electrolyte fuel cell (PEFC) is expected to be employed in automobiles. The bipolar plates in the PEFC perform many functions and account for a significant portion of the total weight, volume and cost of the PEFC. Metal-based materials have received great attention as an alternative to the traditional carbon-based materials for bipolar plates. The PEFC environment to which bipolar plates will be exposed is a very aggressive corrosion condition for metals. This is because the hot water of about 353 K generated by the cell reaction dissolves the solid electrolyte to form H⁺ and F⁻ ions.1,2)

In this work, we focused on the properties of titanium as a bipolar plate. It has excellent corrosion resistance in an acidic environment and a high strength to weight ratio. The electrochemical properties of titanium have been widely studied by many researchers.3–24) Titanium forms a surface oxide film with low conductivity, which may decrease the performance of the PEFC due to the increase in contact resistance. The corrosion resistance of titanium is significantly affected by fluoride concentration and pH.16–22) Some researchers examined the corrosion behavior of titanium under the PEFC conditions and found that titanium has high corrosion resistance but has high contact resistance.25–27) However, there is no examination on the growth behavior of oxide films on titanium in PEFC environments and on the relationship between the film properties and the contact resistance. The objective of this work is to investigate the electrochemical properties of titanium, especially the growth behavior of surface oxide films in PEFC environments, and the contact resistance between the Ti surface and carbon cloth.

2. Experimental

2.1 Specimens and electrolytes

Commercially available pure titanium sheets with a mirror finish (Tokyo Stainless Grinding Co., Ltd.) were cut into disk specimens with a diameter of 15 mm or 22 mm. Before the experiment, the specimens were ultrasonically cleaned in acetone and dried in a nitrogen stream. The specimen was then mounted on a Cu current holder by a PTFE fitting cap and a Valflon® O-ring inside the cap.

The electrolyte used was 1 mol·m⁻³ H₂SO₄ containing 0, 80 × 10⁻³ and 800 × 10⁻³ mol·m⁻³ LiF (pH = 2.7) at 353 K. In-situ ellipsometry and electrochemical impedance spectroscopy were performed in 1 mol·m⁻³ H₂SO₄ containing 80 × 10⁻³ mol·m⁻³ LiF at 353 K.

2.2 Potentiodynamic polarization measurement

Potentiodynamic polarization curves were measured using a conventional three electrode cell. A Pt plate and an Ag/AgCl(3.33 kmol·m⁻³ KCl) electrode were used as the counter and reference electrodes, respectively. The potential was scanned at a constant rate of 3.8 × 10⁻⁴ V·s⁻¹. Unless otherwise indicated, all potentials in this paper are expressed relative to the Ag/AgCl(3.33 kmol·m⁻³ KCl) electrode. We measured polarization curves in O₂ saturated solutions over the potential range from the OCP (open circuit potential) to 1.5 V in order to examine the electrochemical properties of titanium in PEFC cathode conditions. The polarization curves were also measured in a similar manner in H₂ saturated solutions at potentials below 0 V in order to focus on the PEFC anode conditions. Test solutions were bubbled with O₂ or H₂ for 1 h before the experiment. After heating the solution up to 353 K, the specimen was immersed for 2000 s under the OCP condition, and then polarization was started. The solution was bubbled with the gases throughout the experiment. The polarization measurement was performed in 1 mol·m⁻³ H₂SO₄ containing 0, 80 × 10⁻³ and 800 × 10⁻³ mol·m⁻³ LiF at 353 K. The highest fluoride concentration employed (800 × 10⁻³ mol·m⁻³) is relatively high as a PEFC condition, but is used to examine the influence of fluoride ions on the electrochemical behavior of titanium.

2.3 In-situ ellipsometry

The growth behavior of surface films on the specimen under the simulated PEFC operating conditions was examined by in-situ ellipsometry. A rotating-analyzer automatic...
ellipsometer, an electrolyte cell with two optical windows and a conventional three electrode potentiostat were used. A Pt plate and a Pt wire with platinum black were used as the counter and reference electrodes, respectively. Monochromatic light of wavelength 546.1 nm was used as the incident light and the angle of incident was set at 60.0°. From the relationship between the intensity of reflected light and the angle of an analyzer, two ellipsometric parameters, the relative phase retardation, \( \Delta \), and the relative amplitude of reduction, \( \Psi \), were measured. The thickness and optical constant of the surface films were determined using a theoretical \( \Delta \) vs. \( \Psi \) curve which fitted the experimental \( \Delta \)-\( \Psi \) data with minimal error. The theoretical \( \Delta \) vs. \( \Psi \) curves were calculated using Drude’s exact optical equations for a threemedium (ambient-film-substrate) model. To simulate the operating conditions of the PEFC anode and cathode electrodes, the test solution (1 mol-m\(^{-3}\) H\(_2\)SO\(_4\) + 80 \times 10\(^{-3}\) mol-m\(^{-3}\) LiF at 353 K) was bubbled with H\(_2\) and O\(_2\), respectively. These gases were carefully injected so as to ensure contact with the Pt reference electrode and to avoid disturbing the optical measurement. The rest potentials of the Pt electrode in the test solution bubbled with H\(_2\) and O\(_2\) were −0.36 V and +0.64 V, respectively. In this work, we refer to these two potential values as the PEFC anode and cathode operating potentials. The specimens were polarized at the same potential as the Pt reference electrode.

2.4 Surface analysis
Field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6500F) was used to characterize the surface morphology of specimens. The chemical composition of surface films was analyzed by X-ray Photoelectron Spectroscopy (XPS, VG Scientific, Theta Probe) with a monochromated Al K\( \alpha \) X-ray source operating at an accelerating voltage of 15 kV, and an anode current of 30 mA. The working pressure of the system was less than 5.0 \times 10^{-6} Pa. The X-ray spot size was set to 200 \( \mu \)m. Ti 2p, O 1s, C 1s and F 1s electron orbital spectra were measured. The spectra were collected at 32 different take-off angles over the range from 23.95° to 82.06° by a multi channel detector. The photoelectron binding energy was calibrated using the C 1s peak appearing at 285.0 eV in the background spectra. Ti 2p spectra were compared with the reference spectra taken from standard materials. As standard materials, reagent grade chemicals of TiO\(_2\) (Rutile: 99%, Anatase: 98.5%), Ti\(_3\)O\(_7\) (99.9%), TiO\(_2\) (99.9%), TiH\(_2\) (99%), and LiF (98%) were used.

2.5 Electrochemical impedance spectroscopy (EIS)
In order to investigate the electrochemical reaction kinetics, EIS measurements were performed under the simulated PEFC conditions using a frequency response analyzer (FRA, NF Corporation, FRA5022). The frequency range was 100 kHz to 1 mHz. The specimens were polarized at the operating potentials of PEFC, −0.36 V (anode condition) and 0.64 V (cathode condition) by a conventional three electrode potentiostat with a Pt counter electrode and an Ag/AgCl(3.33 kmol m\(^{-3}\) KCl) reference electrode. A sinusoidal a.c. voltage with an amplitude of 20 mV peak-to-peak was superimposed on the d.c. polarization potential.

2.6 ICP-AES analysis
It is difficult to determine anodic dissolution rate of titanium from the current density measured under the PEFC anode condition because titanium lies in cathodic polarization region. Therefore the amount of titanium species dissolved into the solution was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Titanium was potentiostatically polarized under the simulated PEFC anode condition and the electrolyte was sampled after 0, 1, 10, 24, and 72 h polarization and served for ICP-AES analysis.

2.7 Contact resistance measurement
Bipolar plates play an important role to transfer electrons generated at the PEFC anode electrode of one cell to the cathode electrode of the next cell. Therefore, the contact resistance at the interface between the bipolar plate and gas diffusion layer is required to be low. In this work, the contact resistances between the carbon cloth (C.C.) (Toray EC-CC1-060T, thickness: 400 \( \mu \)m) and the specimen, \( R_{\text{C.C./S}} \), was measured by a four-probe method with a TSURUGA model 5022 resistance meter. A schematic illustration of the experimental assembly is shown in Fig. 1. The compaction force applied to the assembly was scanned from 50 N to 360 N at a constant rate of N-S\(^{-1}\). The apparent contact area between the carbon cloth and the specimen was 1 \times 10^{-4} m\(^2\). The total electrical resistance of the assembly shown in Fig. 1, \( R_{\text{Total}} \), is given by eq. (1).

\[
R_{\text{Total}} = R_{\text{C.C./S}} + R_{\text{S/Au}} + R_{\text{C.C.}} + R_{\text{S}}
\]

Where \( R_{\text{C.C./S}} \) and \( R_{\text{S/Au}} \) stand for the contact resistance between the carbon cloth and the specimen surface and that between the rear side of the specimen and the Au probe, respectively. \( R_{\text{C.C.}} \) and \( R_{\text{S}} \) express the bulk resistance of the carbon cloth and the specimen, respectively. We evaluated \( R_{\text{C.C./S}} \) from measured \( R_{\text{Total}} \) under the assumption that the values of \( R_{\text{S/Au}}, R_{\text{C.C.}} \) and \( R_{\text{S}} \) can be regarded as negligible.

3. Results and Discussion

3.1 OCP measurement
Figure 2 shows changes in OCP as a function of time. Both the concentration of fluoride ions and the kind of bubbling gas were shown to affect the OCPs of Ti. The OCPs decrease with increasing fluoride concentration, and at a given fluoride concentration, they increase with O\(_2\) bubbling. This indicates
that fluoride ions increase the anodic partial current due to the dissolution of Ti, and O₂ increases the cathodic partial current due to O₂ reduction. When the solution contained 800 × 10⁻³ mol·m⁻³ fluoride and was saturated with H₂, Ti was depassivated. The fluoride concentration less than 80 × 10⁻³ mol·m⁻³, which is generally employed as the concentration simulating a real PEFC condition, did not cause depassivation of Ti even when the solution was bubbled with H₂.

3.2 Polarization curves in O₂ saturated solutions (PEFC cathode condition)

Figure 3 shows the potentiodynamic polarization curves of Ti in the O₂ saturated solutions with various fluoride concentrations. Ti was passivated over a wide range of potential up to 1.5 V. When the fluoride concentration increased, the OCP shifted to a lower potential, and the passive current density increased. This indicates that the higher the fluoride concentration, the higher the anodic partial current of dissolution of Ti. The operating potential of the PEFC cathode electrode was determined by its oxygen reduction reaction (ORR) and was estimated to be around 0.64 V under open circuit conditions. The current densities at 0.64 V are 1.1 × 10⁻², 1.5 × 10⁻² and 2.3 × 10⁻² A·m⁻² for fluoride concentrations of 0, 80 × 10⁻³ and 800 × 10⁻³ mol·m⁻³, respectively. The operating potential of the cathode under loading conditions is generally lower than 0.64 V. It has been reported that under extraordinary operating conditions, where localized hydrogen starvation occurs, the potential difference between the anode and cathode increases to 1.44 V.²⁰ The observed high stability of Ti over the wide potential range of up to 1.5 V is a great advantage from the perspective of durability, especially when compared to other metals like stainless steel.

3.3 Polarization curves in H₂ saturated solutions (PEFC anode condition)

Figure 4 shows the potentiodynamic polarization curves of Ti in H₂ saturated solutions with various fluoride concentrations. In 0 and 80 × 10⁻³ mol·m⁻³ fluoride containing solutions, the OCPs became stable at −0.2 and −0.36 V, respectively, and a limiting current region appears between −0.6 and −0.85 V in the cathodic polarization curve. The limiting current is due to the diffusion controlled mass transport of H⁺ ions. Ti was activated in the solution with 800 × 10⁻³ mol·m⁻³ fluoride, where the OCP was stable at −0.9 V. The anodic current increased steeply with increasing potential from the OCP and showed an active dissolution peak at around −0.8 V. It can be seen that the operating potential of the PEFC anode, −0.36 V, lies in the active-passive transition region in the 800 × 10⁻³ mol·m⁻³ fluoride solution. In the case of fluoride concentrations of 80 × 10⁻³ mol·m⁻³ and 0 mol·m⁻³, −0.36 V lies in the anodic-cathodic transition region and cathodic polarization region, respectively.
Although TiO\textsubscript{2} is thermodynamically stable at both the anode and cathode operating potentials in the solution with pH = 2.7, as was expected from E-pH diagram\textsuperscript{30),} the PEFC anode condition might be a problem in the case of titanium since the operation potential is close to the active dissolution region.

### 3.4 In-situ ellipsometry analysis in the PEFC anode condition

Figure 5 shows the experimental and theoretical Δ-Ψ plots for Ti polarized at -0.36 V in 1 mol·m\textsuperscript{-3} H\textsubscript{2}SO\textsubscript{4} + 80 × 10\textsuperscript{-3} mol·m\textsuperscript{-3} LiF at 353 K. The polarization condition simulated the PEFC anode condition. The Δ-Ψ locus from point A (start) to B (42 min) corresponds to the heating-up period under the open circuit condition. During this period, Δ-Ψ plots moved to the upper right direction along the theoretical Δ-Ψ curve with \( N_2 = 2.4 - 0.09i \), which indicates the dissolution of an oxide-film formed in air (air-formed film). When the temperature reached 353 K, potentiostatic polarization at -0.36 V was started (point B). Δ-Ψ plots remained almost unchanged for 20 min after potential was applied. After 20 min passed, Δ-Ψ plots began to move to the left along the theoretical Δ-Ψ curve with \( N_2 = 1.88 - 0.00i \), which indicates the growth of a new surface film. The thickness of the film at each stage of measurement can be read from the thickness scale of the theoretical curves.

Figure 6 shows the changes in the film thickness and current density as a function of time. Ti specimens are initially covered with an air-formed film with a thickness of about 3 nm. The film thickness decreased during the first half hour, and then increased with the lapse of time. This means that the dissolution of the air-formed film is followed by the growth of a new surface film. The film was 21.7 nm thick after 72 h of exposure. The current was anodic during the initial stage of polarization, and then became cathodic after 4 h had passed. The film thickness increased almost linearly with time during the anodic current period, revealing the dissolution of Ti substrate and the growth of a new surface film occur simultaneously. The transition from an anodic current to a cathodic one is thought to be caused by the suppression of anodic dissolution with the growth of the surface film. The current density became constant at around -1.4 × 10\textsuperscript{-3} A·m\textsuperscript{-2} after 24 h, while the film growth continued.

### 3.5 In-situ ellipsometry analysis in the PEFC cathode condition

Figure 7 shows the experimental and theoretical Δ-Ψ plots for Ti polarized at +0.64 V in 1 mol·m\textsuperscript{-3} H\textsubscript{2}SO\textsubscript{4} + 80 × 10\textsuperscript{-3} mol·m\textsuperscript{-3} LiF at 353 K. The polarization condition simulated the PEFC cathode condition. The air-formed film dissolved in a similar manner to the simulated anode condition, during the heating-up period defined between points A (start) and B (44 min). Immediately after the operating potential (0.64 V) was applied at point B, Δ-Ψ plots jumped to point C, which indicates the rapid formation of an anodic oxide film. After that, Δ-Ψ plots remained almost constant. A theoretical curve with \( N_2 = 2.3 - 0.07i \) can be applied to fit the experimental plots.

Figure 8 shows the changes in the film thickness and current density as a function of time. A barrier-type film grew on the specimen because the film thickness increased sharply at the beginning of polarization and then remained almost constant. The film was 5.2 nm thick after 72 h of polarization which is about one fourth of what it was under the anode condition. The anodic current density decreased with time and reached 8.0 × 10\textsuperscript{-5} A·m\textsuperscript{-2} after 72 h.

### 3.6 Surface analysis

Figure 9 shows SEM images of Ti specimens after polarization for 72 h under the PEFC (a) anode and (b) cathode conditions. The surface of Ti polarized under the anode condition was covered with flower-like precipitates,
while that treated under the cathode condition remained apparently unchanged. From the surface appearance shown in Fig. 9(a) and continuous film growth behavior in Fig. 6, dissolution and precipitation is thought to be a predominant mechanism for film growth under the PEFC anode condition.

XPS spectra were obtained on the specimen with three different conditions, (a) after 72 h polarization under the PEFC anode condition, (b) after 72 h polarization under the PEFC cathode condition and (c) as received. Ti 2p XPS spectra of specimens (b) and (c) depended on the detection angle of the photoelectrons. That is, as the detection angle decreased, the strong peak at 458.8 eV slightly shifted toward the low binding energy side and a weak peak appeared at 454 eV, which can be attributed to Ti metal. To ascertain the average film composition we binned all XPS spectra measured at different detection angles and performed peak deconvolution using reference spectra measured for standard materials. The results are shown in Fig. 10. The film formed under the PEFC anode condition (Fig. 10(a)) is composed mainly of TiO$_2$. The films formed under the cathode condition (Fig. 10(b)) and in air (Fig. 10(c)) are composed of TiO$_2$ and suboxides such as TiO. The peak due to Ti metal was detected, as is shown in Fig. 10(b) and (c). Therefore, a suboxide might exist in the inner region close to the film-metal interface. O1s spectra consist of three components, M-O (M: metal), M-OH and H$_2$O or CO$_2$. The M-O component is predominant in all the specimens. No signal of F 1s and S 1s was detected, indicating that no fluorides and sulfides are incorporated from the solution into the surface films.

3.7 Electrochemical impedance spectroscopy (EIS)

Figure 11 shows the typical impedance spectra of Ti under the simulated PEFC anode and cathode conditions. All the spectra obtained in this work showed simple capacitive characteristics, while the slope of log $|Z|$ vs. log $f$ plot measured after 72 h polarization under the anode condition was lower than an ideal value of $-1.0$. This deviation might be attributed to roughness and/or non-uniformity of electrode surface, as can be seen in the SEM image (Fig. 9(a)). In order to obtain approximate values of capacitance, the experimental data were fitted using a simple a Randles type equivalent circuit, as shown in Fig. 12, where $R_{\text{sol}}$ means the solution resistance, $R_p$ the polarization resistance and $C_e$ the electrode capacitance.

Figure 13(a) shows the change in $R_p$ as a function of time in the simulated PEFC environments. The values of $R_p$ obtained under the cathode condition are more than one order of magnitude higher than those measured under the anode condition. This suggests that the barrier-type film formed under the cathode condition suppressed the charge transfer reaction at the film-solution interface. Figure 13(b) shows the change in $C_e$ as a function of time. The value of $C_e$ in the cathode condition remained approximately constant at ca. 0.2 F m$^{-2}$. Under the anode condition, $C_e$ increased as time passed and reached ca. 2.6 F m$^{-2}$ after 72 h. This is due mainly to the large surface area of the film formed by the dissolution-precipitation processes and partly to the presence of a thin compact oxide layer underneath the precipitated film. The $R_p$ for the specimen under the anode condition remained almost unchanged after 3 h despite the continuous film growth, as shown in Fig. 6. The film formed under the anode condition does not effectively suppress the electrochemical reaction on the surface of Ti.

3.8 ICP-AES analysis

No titanium species were detected in the ICP-AES analysis after 0 to 72 h polarization under the PEFC anode condition. It was confirmed that the lower detection limit of titanium
was as low as $1.0 \times 10^{-5}$ mol·m$^{-3}$, since the atomic emission peak of titanium at 344 nm was clearly detected from the reference solution containing $1.0 \times 10^{-5}$ mol·m$^{-3}$ Ti$^{4+}$ and $8.0 \times 10^{-3}$ mol·m$^{-3}$ LiF. The result indicates that the concentration of Ti in the test solutions is lower than $1.0 \times 10^{-5}$ mol·m$^{-3}$. Since Ti(IV) species are thermodynamically stable at the PEFC anode potential, titanium dissolves by reaction (2).

$$\text{Ti} + \text{H}_2\text{O} \rightarrow \text{TiO}^{2+} + 2\text{H}^+ + 4\text{e}^-$$  (2)
Then, TiO\(^{2+}\) undergoes hydrolysis reaction (3) to form TiO\(_2\) precipitates.

\[
\text{TiO}^{2+} + \text{H}_2\text{O} = \text{TiO}_2(\downarrow) + 2\text{H}^+ \quad (3)
\]

The equilibrium concentration of TiO\(^{2+}\) in the solution of pH2.7 is \(1.0 \times 10^{-16.7}\) mol m\(^{-3}\) and \(1.0 \times 10^{-6.6}\) mol m\(^{-3}\) for non-hydrous and hydrous TiO\(_2\), respectively. We suppose that TiO\(_2\) precipitates as a partially hydrated form. The formation of TiO\(_2\) films by a dissolution-precipitation mechanism is responsible for the absence of Ti(IV) species in the electrolyte and the observed high grow rate of surface films.

### 3.9 Corrosion behavior and dissolution rate of titanium in the PEFC conditions

Since partial anodic current densities of Ti in the PEFC anode condition were difficult to be determined by the ICP-AES analysis of the test solutions, they were calculated by the surface oxide film growth rates shown in Fig. 6. In the calculation, the surface film was assumed to be composed of TiO\(_2\) rutile and void because the refractive index of the surface film (1.88) was much lower than that of TiO\(_2\) rutile (2.67). The volume ratio of TiO\(_2\) was calculated to be 47% by Braggmann’s effective medium approximation (EMA). The oxide film growth behavior observed in Fig. 6 can be roughly divided into two stages, I and II. Stage I corresponds to the period of 0.6–4 h, and is characterized by the appearance of anodic current and a high film growth rate. Stage II, corresponding to the period of 4–72 h, can be characterized by the appearance of cathodic current and a low film growth rate. If we assume that the film thickness vs. time relationship is linear, i.e., the film growth rate is constant in each stage, we can estimate the partial anodic current density of Ti at \(5.55 \times 10^{-2}\) and \(0.49 \times 10^{-2}\) A m\(^{-2}\) in stage I and II, respectively. Thus estimated anodic current density is much higher than that of PEFC cathode condition, suggesting the less protectiveness of surface oxide films under the PEFC anode condition. The anodic current density in stage II was lower than the recommended value (<1 \(\times 10^{-2}\) A m\(^{-2}\)) by United States Department of Energy (DOE). Electrochemical behaviors of titanium in the PEFC anode conditions are schematically summarized in Fig. 14. Because of a low polarization potential in the anode condition, a pre-existing native oxide film is not stable, which results in a relatively high anodic current at the initial stage of polarization. Titanium species dissolve into the solution and precipitate on the surface of Ti as TiO\(_2\) (Stage I). The surface is gradually covered with a precipitated film, which suppresses both the dissolution and precipitation rates. The sign of current density turns from anodic to cathodic. The precipitated film is porous and less effective for the complete protection of the Ti substrate, resulting in continuation of the dissolution-precipitation process on Ti (Stage II).

In the PEFC cathode condition, titanium is stable due to the formation of a barrier-type compact oxide film. The dissolution rate of titanium in the steady state condition is given by the anodic current density. As shown in Fig. 8, the steady state anodic current density became \(8.0 \times 10^{-5}\) A m\(^{-2}\) which is significantly smaller than the recommended value by DOE.

### 3.10 Contact resistance measurement

Figure 15 shows changes in the contact resistance, \(R_{\text{CC/S}}\), as a function of compaction force (CF). Three different
specimens were used: (a) titanium after 72 h polarization under the PEFC anode condition, (b) after 72 h polarization under the PEFC cathode condition and (c) as-received. The contact resistance decreased exponentially with increasing compaction force.

The contact resistance of the specimen (a) showed almost the same value as that of the specimen (b) in the high compaction force region despite the fact that the surface film on the specimen (a) is thicker than that on the specimen (b). The relatively low value of $R_{\text{C.C.}/S}$ for the specimen (a) can be attributed to the rough surface profile as shown in Fig. 9(a). The contact resistance of the specimens (a) and (b) at the same compaction force of 1.40 MPa is $274 \times 10^{-7}$ Ω·m² and $285 \times 10^{-7}$ Ω·m², respectively, both of which are much higher than the $10 \times 10^{-7}$ Ω·m² recommended to be achieved at 1.0–1.50 MPa for a practical PEFC. $R_{\text{C.C.}/S}$ is in inverse proportion to the real area of contact, $A_R$, if the electrical resistance of current constriction at the interface is negligible. Assuming this is the case, $A_R$ increase exponentially with CF. The contact resistance became ca. $71 \times 10^{-7}$ Ω·m² at 3.60 MPa for both specimens (a) and (b), which indicates that the contact resistance can be decreased significantly when a large $A_R$ value is achieved even in the presence of a surface oxide film.

4. Conclusions

(1) The PEFC cathode operating potential, $+0.64$ V, lies in the anodic polarization region and the anode operating potential, $-0.36$ V, in the cathodic region or the cathodic to anodic transition region for titanium exposed to 1 mol·m⁻³ H₂SO₄ containing 0 to 800 $\times 10^{-3}$ mol·m⁻³ LiF.

(2) The anodic dissolution of titanium accelerates as the fluoride concentration increases in both the H₂ and O₂ saturated 1 mol·m⁻³ H₂SO₄ solution.

(3) Under the simulated PEFC anode condition, an air-formed film dissolves and a new surface film mainly composed of TiO₂ forms by a dissolution-precipitation mechanism up to 20 nm after 72 h. The film is characterized by rough surface morphology, low polarization resistance and low contact resistance. The steady state anodic current density for titanium dissolution was calculated to be $0.49 \times 10^{-5}$ A·m⁻² from the surface oxide film growth behavior. The simulated PEFC anode condition is more aggressive for titanium than the simulated PEFC cathode condition.

(4) Under the simulated PEFC cathode condition, a barrier-type film of up to 5 nm in thickness, composed of TiO₂ and Ti suboxides forms immediately after polarization. The film has high polarization resistance and high contact resistance. The steady state anodic current density was as low as $8.0 \times 10^{-5}$ A·m⁻².

Acknowledgements

This work was supported in part by Global COE Program “Materials Integration (International Center of Education and Research), Tohoku University”, MEXT, Japan.

REFERENCES


![Fig. 15 Changes in the contact resistance, $R_{\text{C.C.}/S}$, as a function of compaction force, $F$, for three specimens: (a) Ti after 72 h polarization under the PEFC anode condition, (b) Ti after 72 h polarization under the PEFC cathode condition and (c) as-received Ti.](image-url)


