

Electrochemical Polishing of Metallic Titanium in Ionic Liquid

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We investigated the electrochemical dissolution of titanium in TMHA-Tf₂N ionic liquid in order to develop a new polishing method for titanium. No dissolution of titanium was observed during the anodic potential sweep up to +6.0 V vs. I₃⁻/I⁻ because of the formation of titanium oxide layer during the potential sweep. But when a certain anodic potential was applied instead of the potential sweep, titanium was successfully dissolved to the extent of detectable weight loss. Moreover, TMHA-Tf₂N ionic liquid indicated fluorescence X-ray of titanium and the titanium surface showed a shiny metallic silver appearance after experiment. We found that the immersed potential of titanium in the ionic liquid became gradually more negative by increasing the number of mechanical polishings before electrochemical experiments. Using the titanium with an immersed potential of more negative than -0.95 V, the titanium was dissolved anodically at +1.6 V. The potential is within the electrochemical window of TMHA-Tf₂N ionic liquid. We believe this technique represents a promising new surface treatment for titanium.

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1. Introduction

Electropolishing of titanium in aqueous solution is difficult because of a strong passive film on the titanium surface. Instead of aqueous solutions an alcoholic solution of perchloric acid is usually used for electropolishing of titanium, with high applied voltage of about 30–60 V.¹⁾ However, since the combination of perchloric acid and alcohol is potentially explosive, an alternative method free from danger is desired. In recent years, ionic liquids (room temperature molten salts)^{2–4)} have been developed as promising electrolytes having a wide electrochemical window.^{5–7)} In this study, we used ionic liquid as a candidate medium for the electropolishing of titanium, and investigated the conditions for anodic dissolution of titanium in detail.

2. Experimental

2.1 TMHA-Tf₂N

We employed an ammonium-imide type ionic liquid, TMHA-Tf₂N whose chemical structure was shown in Fig. 1. It has a quite wide electrochemical window of about 5.6 V.^{8,9)} TMHA-Tf₂N was synthesized by a reaction of TMHA-Br (Tokyo Kasei) with Li-Tf₂N (Fulka).¹⁰⁾ It was dried under vacuum at 120°C for 3 h, and transferred to an Ar-filled glove box where the all electrochemical experiments were carried out.

2.2 Experimental setup and procedure

The two types of electrolytic cells are used in this study; one- and two-compartment cells, as shown in Figs. 2(a) and (b), respectively. The anodic and the cathodic rooms in the two-compartment cell were separated by a sintered glass. All the electrochemical experiments were performed on a three electrode set-up using an electrochemical analyzer (ALS,660A). The electrode potential was measured against

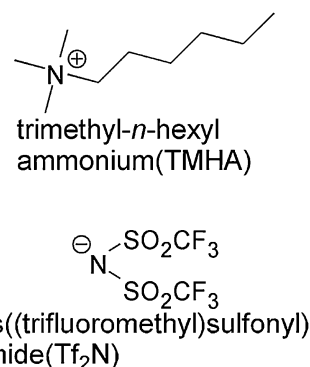


Fig. 1 Chemical structure of TMHA-Tf₂N (trimethyl-n-hexylammonium bis ((trifluoromethyl)sulfonyl)amide).

I₃⁻/I⁻ reference electrode. The I₃⁻/I⁻ reference electrode consists of a platinum wire and a TMHA-Tf₂N solution of 15 mM I₂ and 60 mM (n-C₃H₇)₄NI. Those are contained in a glass tube with a ceramic frit at the bottom. The used working electrode was a titanium, platinum or iron plate as occasion demands, and similarly the counter electrode was a platinum or titanium plate. The titanium plate was mechanically polished using sandpaper in a glove box. The temperature of the solution was kept at 50°C for all the experiments. The elements contained in the ionic liquid after anodic dissolution of titanium were analyzed by an X-ray fluorescence analysis (XRF, XRF-1500; Shimadzu Corporation).

3. Results and Discussion

3.1 General behavior of anodic polarization on titanium

Figure 3(a) is a typical cyclic voltammogram of titanium electrode in the one compartment cell in the potential range from -0.5 V to +6.0 V. The started electrode potential was -0.5 V and it was swept with the scan rate of 10 mV s⁻¹. The cyclic voltammetry was carried out three times for the same titanium electrode without further mechanical polishing. A

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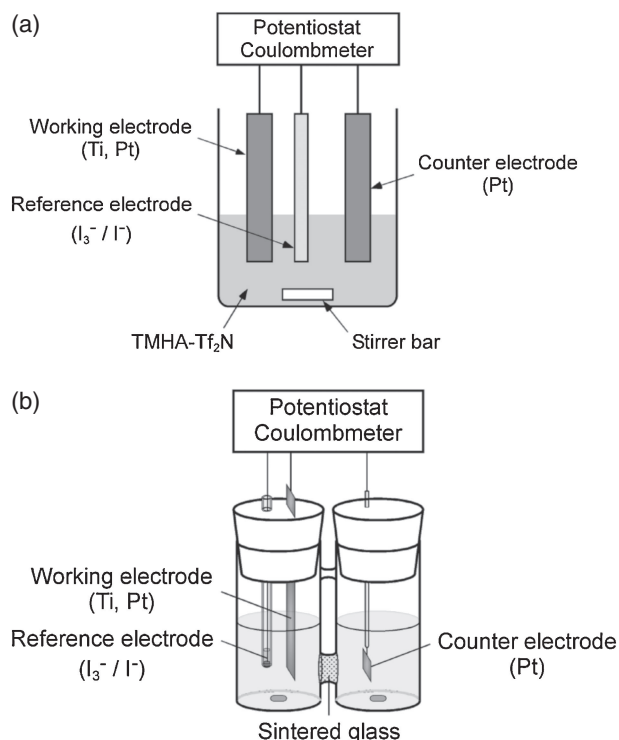


Fig. 2 Schematic illustrations of (a) one-compartment electrochemical cell and (b) two-compartment electrochemical cell.

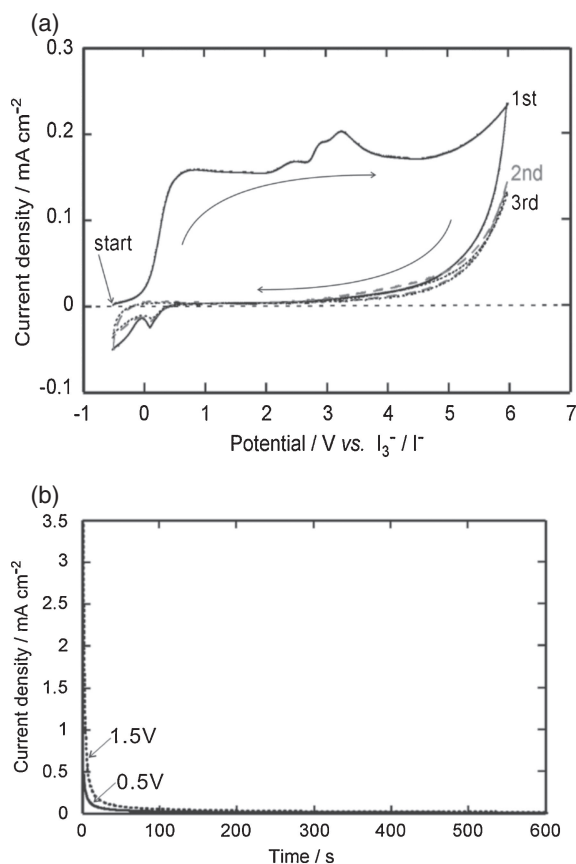


Fig. 3 (a) Cyclic voltammogram of titanium electrode in TMHA-Tf₂N ionic liquid. The titanium electrode was used just after mechanical polishing in a glove box. The scanning rate was 10 mV s⁻¹. (b) Decay of current density of titanium electrode at potentiostatic electrolysis at 0.5 and 1.5 V. The titanium electrode was used just after mechanical polishing in a glove box.

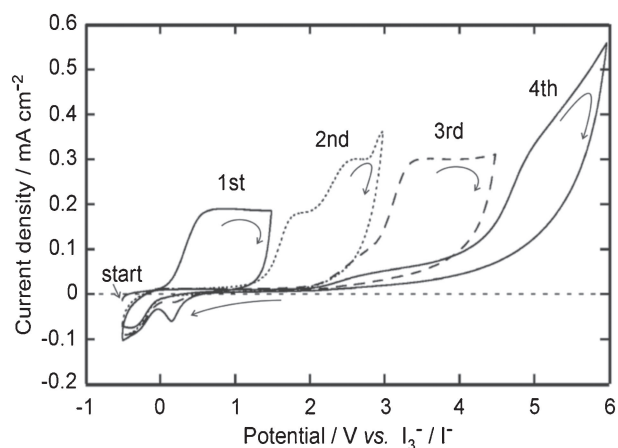
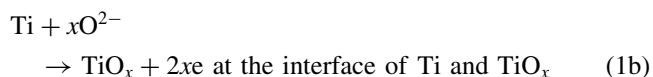
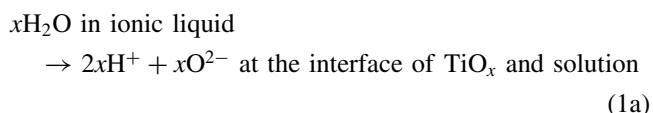


Fig. 4 Variation of cyclic voltammogram of titanium electrode with different switching potentials. The cyclic voltammogram of the 1st cycle was obtained using a titanium electrode just after mechanical polishing in a glove box. Another cycle was obtained after the previous cycle without mechanical polishing. The scanning rate was 10 mV s⁻¹.

constant anodic current of about 0.15 mA cm⁻² was observed only at the first cycle in sweeping potential to higher, but no such constant anodic current was observed in sweeping to lower potential from the switching potential, and in any sweeping during the 2nd and 3rd cycles. Figure 3(b) is the time change of anodic current in the potentiostatic electrolysis of titanium electrode at +0.5 and +1.5 V. The anodic current was initially observed, but it decreased rapidly with time.

Figure 4 shows cyclic voltammograms of a titanium electrode with different switching potentials at each cycle. The titanium electrode behaved as if it had memorized the previous switching potential. That is, the anodic current started to flow just at the switching potential of the previous cycle. These strange behaviors of Figs. 3 and 4 can be understood by assuming a formation of a thin titanium oxide film on the titanium electrode as follows.

First of all, we assume the formation of a thin titanium oxide film on the titanium electrode when the electrode was polarized to positive electrode potential. One item of evidence for this is the color change of the titanium electrode from metallic gray to light gold after polarization from -0.5 V to +6.0 V as shown in Fig. 5. It is well-known that the gold color appears when 10~20 nm of titanium oxide layer forms on titanium.¹¹⁾ The titanium oxide must be a product of anodic electrolysis of water in the ionic liquid because there is no other proper oxygen source in the system. The formation reaction can be written as,



where we assume the formed titanium oxide is TiO_x (*x* is unknown value). In the reaction (1a) a water splits to form protons and an oxide ion on the surface of TiO_x, and then the oxide ion diffuses in the thin film of TiO_x and reacts with Ti

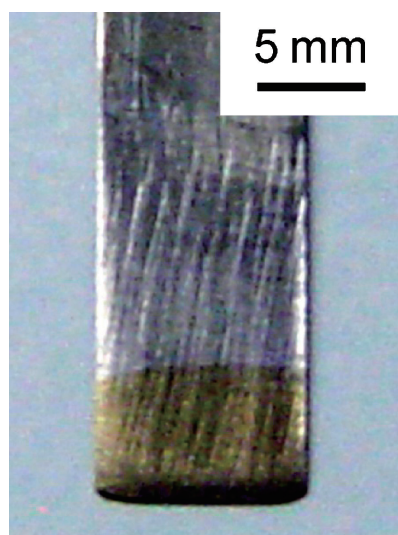


Fig. 5 Photographs of the titanium electrode after sweeping potential from -0.5 V to $+6.0$ V.

as in eq. (1b). This model might be reasonable because diffusion of titanium is probably more difficult than diffusion of oxide ion. We measured the amount of water contamination in TMHA-Tf₂N ionic liquid by the coulometric Karl-Fisher method (MKC-510N; Kyoto Electronics Manufacturing Co., Ltd), and found it was in the range of 50 to 100 mass ppm. We expect that even this small amount of water is sufficient for formation of the thin titanium oxide layer. The thin titanium oxide film has a much higher resistivity than those of titanium metal and ionic liquid. Thus it is a reasonable assumption that a part of the applied voltage is consumed as an ohmic drop (IR drop) in the thin titanium oxide film when current passes through the electrode, and the over potential is smaller than the potential monitored by the electrochemical analyzer. This situation is illustrated in Fig. 6(a). In the figure ϕ^M and ϕ^S are the potentials, defined in physics, of the electrode and the electrolyte close to the electrode, respectively.

When greater potential than the equilibrium potential of $\phi^{M,eq}$ is applied as in case (ii), the over potential, η , for the reaction (1b) should be $\eta = \phi^M - \phi^{M,eq}$ assuming that ϕ^S does not change so much because of small current density. But after the thin oxide film formed as (iii) in Fig. 6(a), the IR drop defined as $V_{IR} = \phi^{S'} - \phi^S$ in the thin oxide film is significant, where $\phi^{S'}$ is the potential in titanium oxide close to the titanium electrode. The over potential for reaction (1b) should be $\eta = \phi^M - \phi^{M,eq} - V_{IR}$. The thickness of the titanium oxide film should be proportional to the amount of electric charge passing through the electrode by eq. (1b). As the resistance of the thin titanium oxide film increases with the thickness of the film, the over potential decreases with time. Finally, when $\phi^M - \phi^{M,eq}$ approaches V_{IR} , the over potential should become zero and the reaction will stop. Meanwhile, when continuously sweeping the potential to higher, the over potential can keep some positive value to allow further formation of titanium oxide film. This situation is illustrated in Fig. 6(b). In the figure, more positive potential is applied in case (iii) than in case (ii). Even though the titanium oxide layer becomes thicker, the over potential

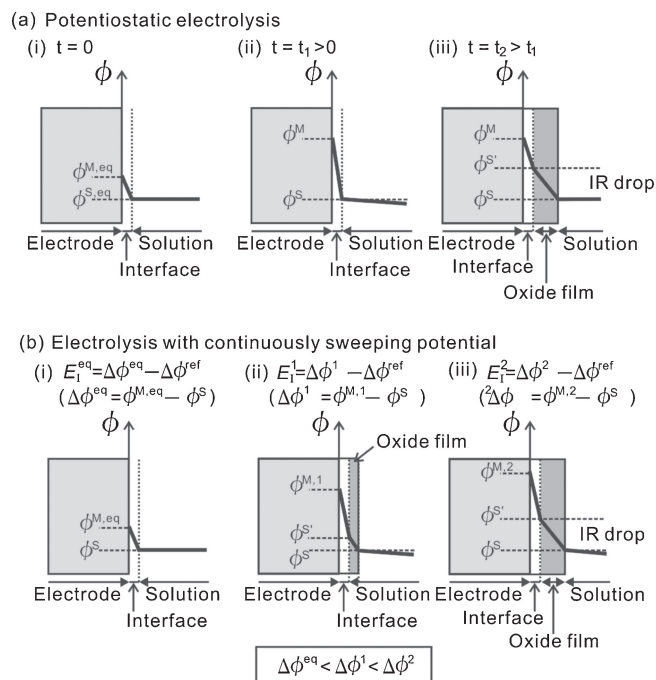


Fig. 6 Schematic diagrams of formation of thin titanium oxide film on titanium electrode by (a) potentiostatic electrolysis and (b) electrolysis with continuously potential sweeping. The figures show that a IR drop in the oxide film become significant. $\Delta\phi^{ref}$ is the potential difference on reference electrode, necessary for definition of electrode potential E_T .

can maintain a positive value for the oxide film to form continuously.

The thin titanium oxide film remains on the titanium surface after the anodic polarization. This means that the electrode memorizes the previous switching potential because a higher potential than the previous switching potential is required to draw current. This mechanism is the reason for the strange behaviors seen in Figs. 3 and 4.

3.2 Potentiostatically anodic dissolution of titanium

Figure 7(a) is the change of current density with time in the potentiostatic electrolysis on titanium at $+9.0$ V in the one compartment cell. The titanium electrode was polished with sandpaper in a glove box, and used as it is; no electrolysis or potential sweep was performed before the electrolysis because the oxide film forms during electrolysis during potential sweep. A large anodic current of about 15 mA cm^{-2} was observed during the electrolysis in the figure. In contrast, only about 0.8 mA cm^{-2} of anodic current was observed when the titanium electrode was polarized gradually from 0 V to $+10$ V as shown in Fig. 7(b). Figure 8(a) is a photograph of the titanium electrode after potentiostatic electrolysis at $+9.0$ V. The color of titanium changed to shiny metallic silver and the weight of the titanium electrode decreased. Titanium K α was confirmed by XRF in the ionic liquid after electrolysis as shown in the figure inserted in Fig. 7(a). The weight loss, the color change to shiny metallic silver, and the presence of titanium ion in ionic liquid clearly indicate that titanium dissolved anodically under the employed conditions. After experiment, the color of the ionic liquid changed to black, which implies partial decomposition of ionic liquid.

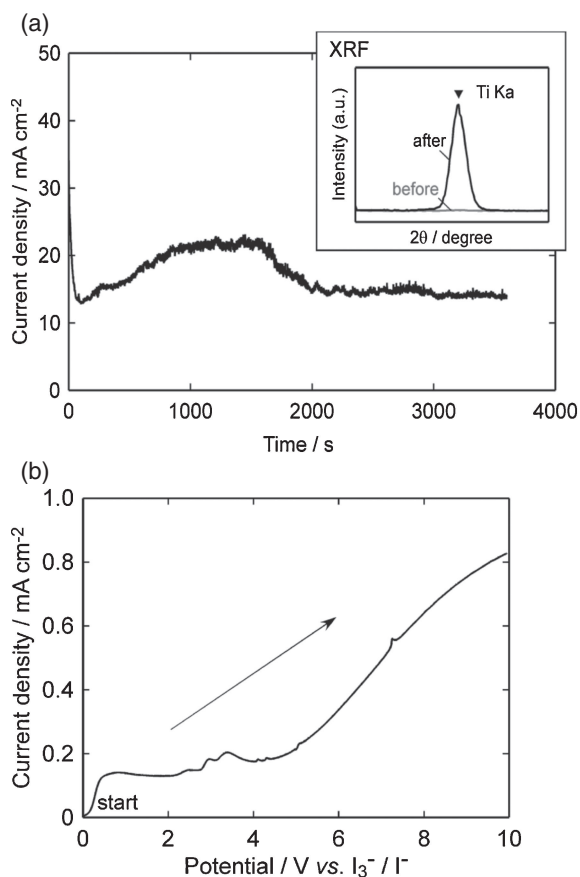


Fig. 7 (a) Time change of current density during potentiostatic electrolysis of titanium electrode at +9.0 V. One component cell was used. The inserted figure is the result of XRF analysis of ionic liquid before and after electrolysis. (b) Linear sweep voltammogram of titanium electrode from 0 V to +10.0 V with the scanning rate of 10 mV s^{-1} . In either experiment, the titanium electrode was used just after mechanical polishing in a glove box.

We then tried to measure the valence of titanium ions dissolved in TMHA- Tf_2N . The relationship between total passed electric charge and weight loss of titanium electrode is shown in Fig. 9. The three lines in the figure are hypothetical lines calculated from the assumption that all of the electric charges are consumed for anodic dissolution of titanium to form a specific ion; divalent, trivalent or tetravalent titanium ions. As a part of the electric charge might be consumed for anodic decomposition of the ionic liquid, the plots should locate below the three lines. However, most of the plots are above the line of tetravalent titanium ions. This implies that the dissolved titanium ion is not tetravalent. Therefore we can say that the titanium ions in ionic liquid would be divalent or trivalent.

3.3 Anodic decomposition of ionic liquid at higher potential

The anolyte of TMHA- Tf_2N ionic liquid after the potentiostatic electrolysis at +10.0 V were investigated. The two-compartment cell was used for potentiostatic electrolysis at +10.0 V to separate anolyte from catholyte, and titanium dissolution was observed at this condition. The photograph in Fig. 10 indicates the color of the ionic liquid

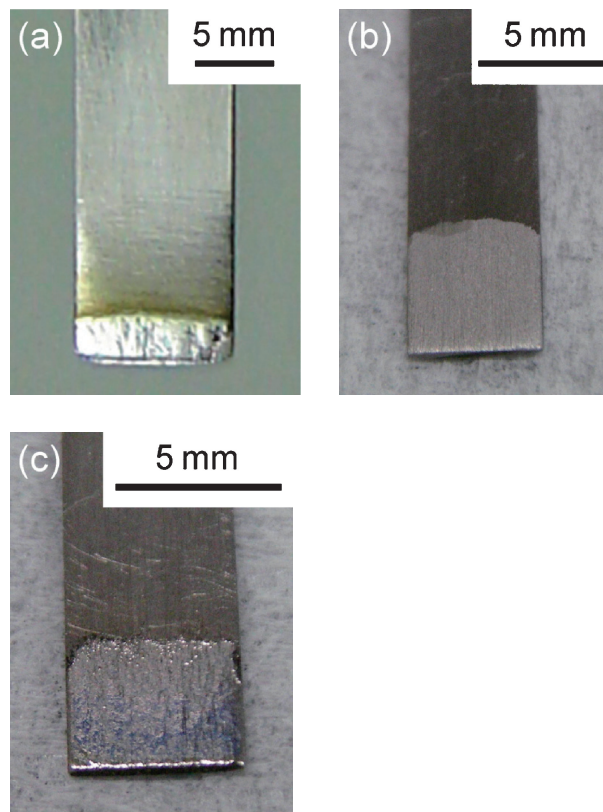


Fig. 8 Photographs of the titanium electrode after potentiostatic electrolysis at (a) +9.0 V, (b) +1.6 V (c) +2.0 V. The well-polished titanium electrodes which exhibit an immersed potential lower than -0.95 V were used for (b) and (c).

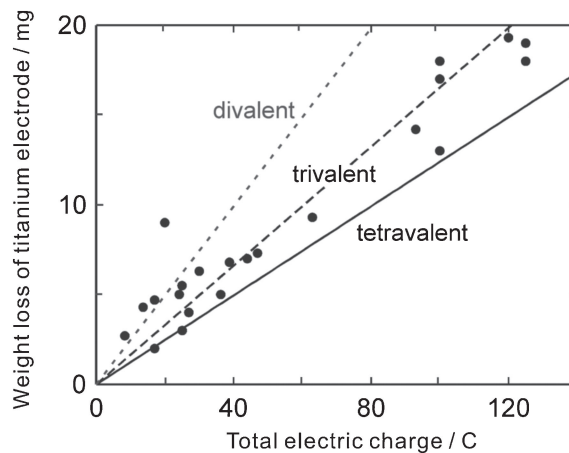


Fig. 9 Relationship between total electric charge and weight loss of titanium electrode during anodic dissolution of titanium. One component cell was used.

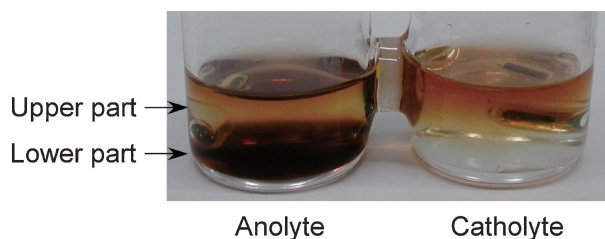


Fig. 10 Photograph of TMHA- Tf_2N ionic liquids in anode and cathode compartments after potentiostatic electrolysis at +10.0 V of mechanically polished titanium electrode.

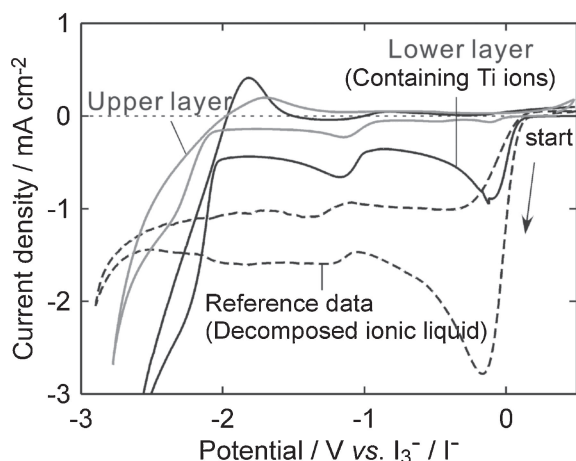


Fig. 11 Cyclic voltammograms of upper and lower layers of anolyte after anodic dissolution of titanium. Platinum plates were used as working and counter electrodes. Scanning rate was 10 mV s^{-1} . The reference data are cyclic voltammograms of anolyte after potentiostatic electrolysis at $+10.0 \text{ V}$ using platinum anode and cathode.

after potentiostatic electrolysis at $+10.0 \text{ V}$. After anodic dissolution of the titanium electrode without any stirring, the ionic liquid in the anolyte separated into two layers; the upper was light transparent brown and the lower was dark brown. Titanium $K\alpha$ was detected only from the lower liquid, indicating the presence of titanium ions there. The color change of the anolyte was obviously due to decomposition of ionic liquid. Figure 11 shows cyclic voltammograms of the upper and lower layers of anolyte. Platinum plates were used as working and counter electrodes. A cathodic bump at around -1.2 V was observed in cyclic voltammograms of both the upper and lower layers of anolyte. Thus, this bump might be related to the anodic decomposition product of the ionic liquid. In addition to this bump, an obvious cathodic peak was observed at around 0 V only in the lower layer of anolyte. A cyclic voltammogram of the anolyte after potentiostatic electrolysis at $+10.0 \text{ V}$ using platinum anode and cathode is shown as reference data in Fig. 11. In this reference experiment, almost the all electric charges on platinum anode were consumed by electrodecomposition of the ionic liquid. Comparing two voltammograms, it is obvious that the cathodic signals at around 0 and -1.2 V are not related to titanium species. Thus, these should indicate the reduction of anodically decomposed products of ionic liquid. As far as we know, the reduction of protons occurs at around 0 V in this ionic liquid.¹²⁾

3.4 Attempts to make the anodic potential for titanium dissolution lower

Titanium was anodically dissolved by the potentiostatic electrolysis at $+9.0$ or $+10 \text{ V}$ but at the same time ionic liquid decomposed on the anode, which is not desirable because of the high cost of ionic liquid. We therefore attempted to make the anodic potential for titanium dissolution less than $+2 \text{ V}$, which is an upper limit of electrochemical windows of TMHA-Tf₂N ionic liquid. Among various trials, we found that the extent of mechanical polishing of titanium before electrolysis is the key to lower

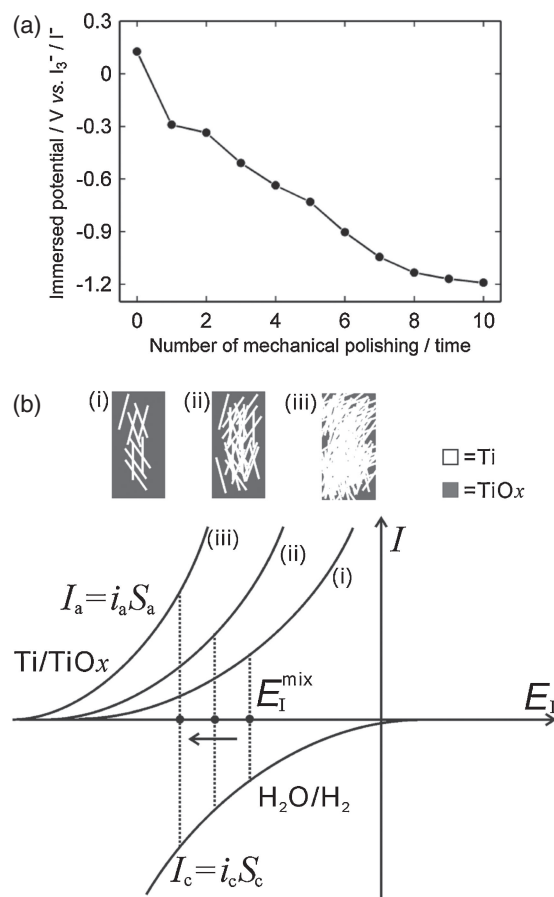
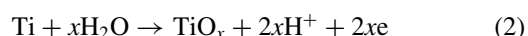


Fig. 12 (a) Decrease of immersed potential of titanium electrode as a function of the number of mechanical polishings. (b) Schematic diagram of the mixed potential with mechanically polished titanium.

the anodic potential for titanium dissolution. So, we introduce some experimental facts and considerations.

Titanium was polished mechanically in the globe box and then immersed in TMHA-Tf₂N ionic liquid. Figure 12(a) shows the relationship between the immersed potential of titanium electrode and number of mechanical polishings. When we increased the number of mechanical polishings, the immersed potential of titanium electrode in ionic liquid became lower. Figure 12(b) depicts how the immersed potential changes. The immersed potential of titanium electrode should be the mixed potential (E_I^{Mix}) determined by following anodic and cathodic reactions.



The partial currents of anodic and cathodic reactions are schematically represented by I_a and I_c in Fig. 12(b). The effective areas of anodic and cathodic reactions are represented by S_a and S_c , respectively. The absolute value of I_a ($= i_a S_a$) is equivalent to I_c ($= i_c S_c$). Illustrated cases (i), (ii) and (iii) in the figure indicate the difference of the extent of mechanical polishing. Case (ii) is more polished than case (i), but less than case (iii). The area of exposed metallic titanium is expected to increase with the number of mechanical polishings. The anodic reaction for oxide formation proceeds preferably on exposed Ti rather than at

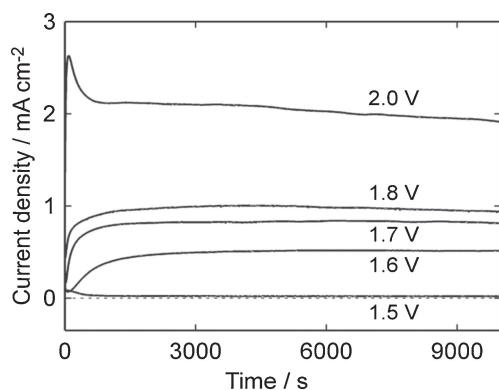


Fig. 13 Result of potentiostatic electrolysis at various potentials. The mechanically polished titanium electrode for which the immersed potential was under -0.95 V was used as the working electrode.

the interface between oxide thin film and titanium because in the latter case the oxide ion diffusion is needed. It is experimentally known that the reduction of protons proceeds despite the presence of thin titanium oxide film. This phenomenon might relate to proton conduction in the thin titanium oxide film.¹¹⁾ So, the cathodic reaction (3) proceeds on exposed Ti and also on the interface between the thin oxide film and titanium. If so, I_a increases with the number of mechanical polishings because S_a is the area of exposed Ti but I_c does not change markedly. Consequently, E_1^{Mix} becomes lower with an increased number of mechanical polishings. Thus, the immersed potential can be used as a parameter indicating the extent of exposed metallic titanium; that is, the titanium electrode with lower immersed potential should have relatively large area of exposed metallic titanium.

We used mechanically-polished titanium with immersed potential of lower than -0.95 V for titanium dissolution experiment. Potentiostatic electrolysis at various potentials was carried out. Figure 13 shows the time change of anodic current in potentiostatic electrolysis at $+1.5$, $+1.6$, $+1.7$, $+1.8$ and $+2.0$ V. A significant anodic current was observed when the potential was higher than $+1.6$ V. Furthermore, the anodic current increased with an increase in the anode potential applied. After electrolysis at potentials higher than $+1.6$ V, the titanium electrode presented the appearance of shiny metallic silver (see Figs. 8(b) and (c)), and the weight loss. However, the color of the titanium electrode treated at $+1.5$ V changed to light gold very slightly and the weight loss of the titanium electrode was not detected. Therefore, we can say that the titanium dissolved anodically at potentials higher than $+1.6$ V, which is within the electrochemical window of used ionic liquid.

4. Conclusion

A titanium oxide film formed on the surface of titanium electrode with sweeping potential to higher potential. A part of the voltage is consumed as an ohmic drop in the thin titanium oxide film when current passes through the electrode, and the over potential on the electrode is smaller than the monitored potential by the electrochemical analyzer. After such a titanium oxide film formed, titanium does not dissolve anodically. But, if the potentiostatic electrolysis is conducted just after the titanium electrode has been polished mechanically in a glove box, titanium can dissolve. Using well-polished titanium which exhibits an immersed potential lower than -0.95 V vs. I_3^-/I^- , the potential for titanium dissolution can be lowered to $+1.6$ V which is in the electrochemical window of TMHA-Tf₂N ionic liquid. Shiny silver titanium was obtained. We believe this technique represents a promising new surface treatment method for titanium.

Acknowledgements

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REFERENCES

- 1) Günter Petzow: *Metallographisches, keramographisches, plastographisches Aetzen*, (Borntraeger Gebrueder, Germany, 1994; Hirohisa Uchida and Haruhisa Uchida translated to Japanese, Nikkan-Kogyo-Sha, Japan, 1997).
- 2) T. Welton: *Chem. Rev.* **99** (1999) 2071–2083.
- 3) M. J. Earle and K. R. Seddon: *Pure Appl. Chem.* **72** (2000) 1391–1398.
- 4) R. D. Rogers and K. R. Seddon: *Science* **302** (2003) 792–793.
- 5) Y. Katayama, S. Dan, T. Miura and T. Kishi: *J. Electrochem. Soc.* **148** (2001) C102–C105.
- 6) F. Endres: *Phys. Chem. Chem. Phys.* **3** (2001) 3165–3174.
- 7) D. L. Boxall and R. A. Osteryoung: *J. Electrochem. Soc.* **149** (2002) E185–E188.
- 8) H. Nakagawa, K. Tsuchimoto, T. Uda, K. Murase and Y. Awakura: *Proc. 11th World conf. on Titanium, Ti-2007 Science and Technology*, Kyoto, Japan, ed. by M. Niinomi, S. Akiyama, M. Ikeda, M. Hagiwara, K. Maruyama, (The Japan Institute of Metals, 2007) pp. 1249–1252.
- 9) K. Murase, K. Nitta, T. Hirato and Y. Awakura: *J. Appl. Electrochem.* **31** (2001) 1089–1094.
- 10) T. Katase, T. Onishi, S. Imashuku, K. Murase, T. Hirato and Y. Awakura: *Electrochem.* **73** (2005) 686–691.
- 11) S. Van Gils, P. Mast, E. Stijns and H. Terryn: *Surf. Coat. Technol.* **185** (2004) 303–310.
- 12) H. Nakagawa, T. Uda, K. Murase and Y. Awakura: *SOHN Int. Symp., Advanced processing of metals and materials volume 3—Thermo and Physicochemical principles*, San Diego, USA, ed. by F. Kongoli and R. G. Reddy, (TMS, The Minerals, Metals and Materials Society, 2006) pp. 641–649.