

Comparison of Corrosion Behaviors of Bare Ti and TiO₂

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Abstract

In this study, titanium (Ti) surface was anodized by applying 60 voltages for two hours to form titanium dioxide (TiO₂) with anodization method. After anodization procedure, comparison of corrosion behaviors of the bare titanium and TiO₂ coated titanium was examined in 1 M KOH solution by using electrochemical methods such as anodic and cathodic current-potential curves and electrochemical impedance spectroscopy (EIS). Cyclic voltammetry (CV) and energy dispersive X-ray (EDX) were used to characterize bare Ti and anodically formed TiO₂ surfaces. According to obtained results, Ti surface was smooth and compact. However, surface structure of TiO₂ coated titanium was porous and nanotubes formed on the surface. This porous structure which has protective layer contributed to increase the corrosion resistance. Higher polarization resistance was obtained on porous TiO₂ than that of bare titanium. Besides, this protective layer bore well against the alkaline corrosion during long-term immersion.

Keywords:

Corrosion;
Titanium;
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1- Introduction

Titanium and its alloys are widely used in many applications, from chemical industry to medical application due to its excellent corrosion resistance which is explained to the thin, stable and protective layer that forms spontaneously on its surface when exposed to the natural environment [1]. Its other important properties are good mechanical strength and high biocompatibility. Recently, many researchers have been investigating the optimization of Ti surface, particularly increasing the thickness of the oxide layer and modifying the surface morphology and crystal structure by using different methods to improve its corrosion resistance and to change chemical structure. Anodic oxidation is one of the most used methods to build anodic films which are long, homogeneous, good electrical properties and porous at high voltages. This protective layer obtained by using anodic oxidation method prevents rapid dissolution of the underlying metal. In addition, Ti possesses a wide potential window during which metal remains in the passive range for this reason, many researchers are interested in anodic oxidation method. Wide passive range is observed not only in acid environment but also in alkaline environment [2]. Growing of TiO₂ layer which is the most homogeneous and best results has been extensively investigated and well established in acid electrolytes [3-5]. However, produced TiO₂ layer tends to dissolve in strong acid electrolytes such as hydrogen fluoride (HF) [6], nitric acid (HNO₃) [7] and hydrogen peroxide (H₂O₂) [8]. To the best of our knowledge, weak acids such as organic acids gave the best results to grow TiO₂ layer [9-13]. Although there is much information of anodic oxidation of metals, up to now less attention is available about corrosion of Ti metal or TiO₂ in strong alkaline solution. In addition, not many systematic works can be found regarding the comparison of corrosion behaviors Ti and oxide layer in alkaline electrolyte until now. When its importance is concerned in many applications, in this study, corrosion behaviors of bare Ti and TiO₂ obtained by using anodization method at high voltage were compared with a series of electrochemical techniques in alkaline electrolyte.

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2- Materials and Methods

Ti disc (grade 2) which is surface area of 0.283 cm^2 is used as a working electrode. All surfaces of Ti electrode is covered with polyester resin except worked surface. Before the anodization procedure, Ti surface was polished by using emery paper (the grid of 320 – 1200). After the polishing, worked surface was washed with deionized water and degreased in acetone, ethanol and deionized water for 10 min, respectively, then dried in air to prepare electrochemical measurements. Ti surface was modified by using anodization solution at constant potential of 60 V for 2 h. Anodization solution consists of 0.5 g NH_4F , 2% (vol.) H_2O and ethylene glycol rest [14]. During the anodization procedure, two-electrode electrochemical cell was used. Pt foil (with 2 cm^2 surface area) as the counter electrode and Ti disc as the working electrode were placed in the cell. The anodization experiment was performed using a direct current (DC) power supply for the fabrication of the TiO_2 . After anodization procedure, Ti electrode with oxide layer was washed with deionized water and was immersed in 1 M KOH solution for electrochemical measurements. Same experiments were done for bare Ti. Three electrode set-up was used for electrochemical measurements which contain Pt and Ag/AgCl as counter and reference electrodes, respectively. Anodic and cathodic current-potential curves were obtained separately after one-hour immersion at E_{ocp} with the scan rate of 1 mV s^{-1} . Polarization resistances of electrodes were determined with EIS method at E_{ocp} after one hour and long-term immersions (30 days). EIS measurements were conducted in the frequency range from 100 kHz to 0.003 Hz and applied amplitude was 0.005 V. Nyquist diagrams obtained from EIS were fitted by using Zview software. Characterization of bare Ti and oxide electrodes were analyzed by cyclic voltammetry (CV) with the scan rate of 100 mV s^{-1} and energy dispersive X-ray (EDX). Electrochemical measurements were carried out by Ivium vertex (model no: V55600) electrochemical analyzer under computer controlled. Nuve BS 30 type water bath was used for controlling the electrolyte temperature ($\sim 25^\circ\text{C}$). Analytical grade chemical substances were used in the experiments and all the experiments were also repeated at least three times.

3- Results and Discussion

Cyclic voltammogram of TiO_2 is given in Figure 1. The cyclic voltammogram of bare Ti is also given in the same figure as the inset. According to the inset, the peak appeared at -1.7 V (Ag/AgCl) is related to the oxidation of hydrogen and transformation of $\text{Ti}^{+3}/\text{Ti}^{+4}$ [13,15]. No oxygen evolution reaction is observed between 0 and 1.0 V (Ag/AgCl) [16]. In the backward scan, the peaks appeared at -1.4 and -1.75 V (Ag/AgCl) indicate the reduction of O_2 and $\text{Ti}^{+4}/\text{Ti}^{+3}$, respectively [15]. For cyclic voltammograms of TiO_2 , the current values of anodic and cathodic peaks are significantly higher than that of obtained on bare Ti and peak potentials shifted to the more positive values. It can be explained that existence of the TiO_2 on the Ti surface greatly enhance its surface area [17]. As it can be seen from Figure 1, characteristic peaks of Ti are clearly observed and no peaks of other metals are seen. In addition to measurements of CV for characterization, EDX analysis of TiO_2 layer on Ti surface is carried out and elemental analysis is found as % 56.52 for oxygen, 27.61 for Ti and 15.87 for F atoms (the spectrum of EDX is not given here). Result of EDX is supported the results of CV.

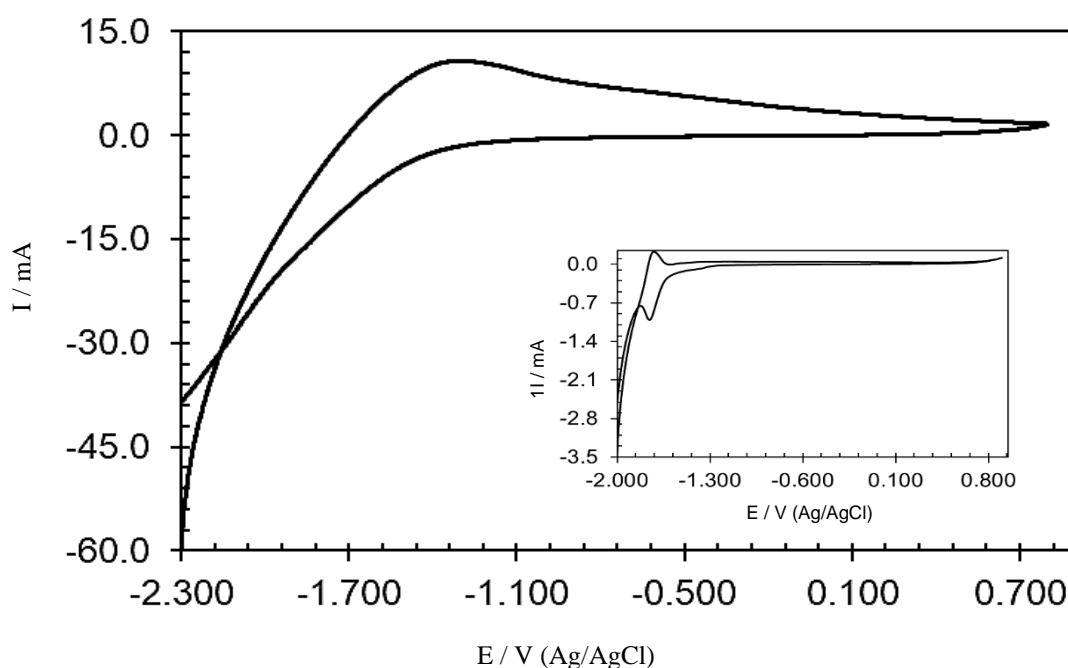


Figure 1. Cyclic voltammogram of TiO_2 obtained by applying the anodization potential of 60 V for 2h. Inset shows the cyclic voltammogram of bare Ti (electrolyte: 1.0 M KOH and scan rate v : 100 mV s^{-1}).

Anodic(a) and cathodic(b) current-potential curves of bare Ti and anodized Ti electrode were given in Figure 2. In the cathodic branch, only hydrogen evolution is seen on both electrodes. When Ti surface is modified with TiO_2 , open circuit potential shifted more positive values and higher hydrogen evolution current density is obtained. According to anodic branch, same behaviors are seen for both electrodes. TiO_2 formed naturally on bare Ti dissolved initial stage for bare Ti, after that, anodic current was constant until $-0.584 \text{ V (Ag/AgCl)}$. Very protective TiO_2 layer formed between these potentials [2,18]. When compared with anodized Ti (TiO_2), anodized Ti reduced the anodic current values. This reducing can be explained with existence of protective TiO_2 layer. This protective oxide layer prevented the Ti surface against attacking of the corrosive alkaline solution. EIS is useful method to understand the metal/solution or oxide/solution interface [19]. For this purpose, EIS analysis is performed for bare Ti and TiO_2 . Nyquist diagrams of bare Ti and anodized Ti are given in Figure 2c. Nyquist diagrams are fitted and parameters are given in Table 1. Two-time constant were obtained on bare Ti and anodized Ti after one hour immersion due to capacitive and typical passive response. Two-time constant shows the existence of bi-layered oxide structures which one is porous outer layer and another is barrier inner layer on the electrode surface [20, 21]. Higher polarization resistance ($R_p=R_1$, porous layer resistance + R_2 , barrier layer resistance) which is nearly twofold was obtained on anodized Ti electrode. This high R_p value proved the existence of the protective passive layer on Ti.

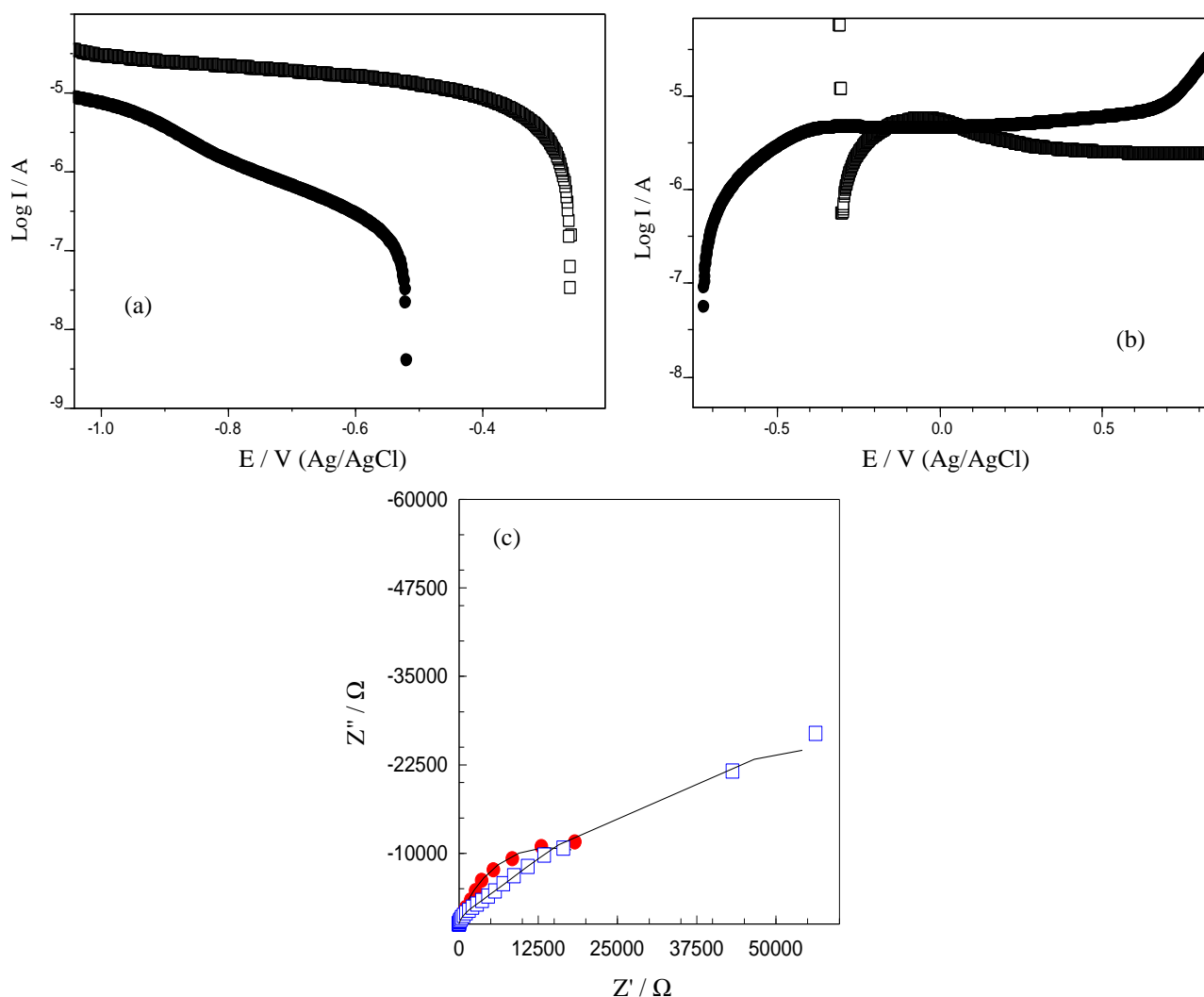


Figure 2. Anodic (a) and cathodic (b) current-potential curves and Nyquist diagrams (c) of bare Ti (●) and anodized Ti (□) in 1 M KOH solution.

To investigate the effect of immersion time on the corrosion behaviors of bare Ti and anodized Ti, EIS measurements are also performed. Figure 3 shows the Nyquist diagrams obtained different immersion times of bare Ti (a) and anodized Ti (b) in 1 M KOH solution. Suggested electrical circuits and fit parameters were given in the same figures as the inset and Table 1, respectively. Since anodized Ti had more porous structure than bare Ti, parallel connected electrical circuit was used [22]. It is seen from Table 1, R_p of bare Ti reduced with increasing immersion time according to 2.day, however R_p values of anodized Ti increased firstly and decreased then increased at 30.day due to protective passive layer. Here, CPE corresponds to constant phase element, CPE is used during fitting instead of double layer capacitance (C_{dl}) as the double layer is not an ideal capacitor [23]. n is phase shift.

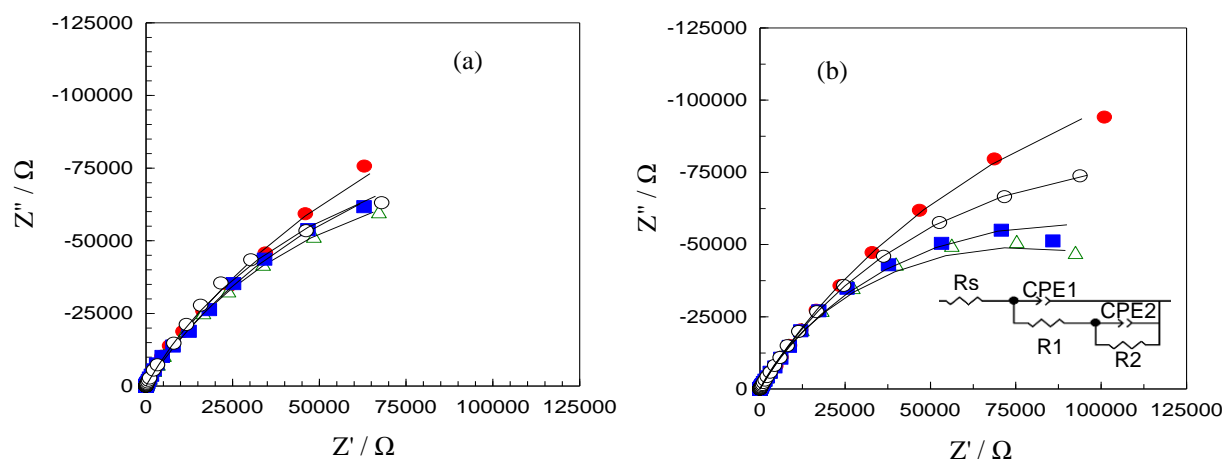


Figure 3. Nyquist diagrams obtained 2(●), 12(△), 22(■) and 30(○) days immersion time of bare Ti (a) and 2(△), 12(●), 22(■) and 30(○) days immersion time of anodized Ti (b) in 1 M KOH solution. Suggested electrical circuits were given as the inset.

Table 1. Fit parameters determined from EIS

Immersion time	Ti					Anodized Ti (TiO ₂)				
	R _p (Ω)	CPE ₁ (F cm ⁻²)x10 ⁻⁵	n ₁	CPE ₂ (F cm ⁻²)x10 ⁻⁵	n ₂	R _p (Ω)	CPE ₁ (F cm ⁻²)x10 ⁻⁵	n ₁	CPE ₂ (F cm ⁻²)x10 ⁻⁵	n ₂
1.hour	36942	26.15	0.70	5.62	0.99	63414	21.45	0.47	1.38	0.95
2. day	343991	18.23	0.69	4.63	0.94	155158	4.84	0.73	8.73	0.75
12. day	203332	19.29	0.71	2.40	0.98	388928	10.07	0.65	7.21	0.75
22. day	214704	20.64	0.71	1.24	0.98	180854	3.14	0.72	11.10	0.71
30. day	263924	20.71	0.72	1.02	0.99	255563	1.94	0.59	12.58	0.73

4- Conclusion

Naturally formed TiO₂ on Ti electrode can prevent the metal against the alkaline corrosion, but this thin layer dissolved in strong alkaline solution. Porous TiO₂ layer was formed on commercial Ti with the anodization method at potential of 60 V for 2 h. Synthesized TiO₂ was characterized by CV and EDX. Appearance of characteristic peaks of Ti confirmed the porous TiO₂ layer on the Ti surface. Anodically formed TiO₂ layer reduced the anodic current and improved the polarization resistance of bare Ti due to existence of porous and protective TiO₂ layer in strong alkaline solution. Anodically formed TiO₂ layer should be used in industrial applications to prevent bare Ti against corrosion..

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6- Conflict of Interest

The authors declare no conflict of interest.

7- References

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