

DOI: 10.21767/2471-9838.100024

Sealing Holes of an Anodic Aluminum Oxide Alloy by Nanotitania for Enhanced Corrosion Resistance

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Abstract

This study aims to explore an effective, novel, and environmentally friendly method that overcomes the limitations and shortcomings existing in the traditional approaches for sealing holes on aluminum alloy. Herein, the hole-sealing treatment of an Anodic Aluminum Oxide (AAO) alloy film using two types of titanium sources with a high stability in aqueous electrolytes, that is, ammonium fluorotitanate and titanium potassium oxalate, to electrically deposit nanotitania on the film surface was investigated. The nanotitania deposited electrochemically for hole sealing has the advantages of the high physiochemical stability, low cost, and non-toxicity, which can thus readily improve the corrosion resistance of the sealed AAO in an environmentally friendly manner. Such sealed AAO can also result in a UV-shielding performance due to the commonly-known UV absorption properties of nanotitania. The hole sealing effect is also compared between the two systems involving the two types of titanium sources at different concentrations, voltages and time. The optimization of the preparation conditions is achieved by means of weight loss measurements. Potentiodynamic scan and electrochemical impedance spectroscopy results reveal that the hole-sealed sample-based on ammonium fluorotitanate shows a higher corrosion resistance as compared to the one based on titanium potassium oxalate. Significantly, the optimal conditions for the hole sealing of the aluminum alloy are evidenced to be the concentration of ammonium fluorotitanate of 0.1 mol/L, AC voltage of 3 V, and time of 900 s.

Keywords: Anodic Oxidation of Aluminum Alloy; Electrical Deposition; Hole Sealing; Titania

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Citation: Chang M, Wei H, Chen D, et al. Sealing Holes of an Anodic Aluminum Oxide Alloy by Nanotitania for Enhanced Corrosion Resistance. *Nano Res Appl.* 2017, 3:2.

Received: June 21, 2017; **Accepted:** July 01, 2017; **Published:** June 04, 2017

Introduction

As the second large category of metallic materials, aluminum and its alloys have been used extensively in the research and engineering industries, just following after iron and steel [1-4]. This is because of their light weight, high specific strength, and superior physical and chemical properties [1,2]. As a result, there are various promising applications for them, e.g., in architecture, automobile, and decoration [5-8]. Generally, anodic oxidation is employed for fabrication of such aluminium alloys, which can result in a highly porous oxidation film [9]. Such a film possesses a strong physical adsorption capability and a high chemical reactivity, facilitating the adsorption of air pollutants and hence causing the corrosion of aluminum plates [10,11]. The anodic

oxidation film of the aluminum alloys exhibits a honeycombed porous structure, with a rather low average pore diameter. It has also been reported that the number of pores can reach as high as $7.7 \text{ mm}^2 \times 10^8 \text{ mm}^2$. Therefore, the hole filling technology is urgently needed to enhance the corrosion resistance, anti-pollution and electrical insulating properties, keeping the surface of the aluminium alloys in a good state [12].

Among the commonly-used methods for sealing the holes of the oxidation film of aluminum alloys, including hydrothermal and metal-salt solution sealing, etc. [13-16], hydrothermal sealing is the most commonly-used one due to its good sealing effect that can also be easily achieved by placing the porous oxidation film into hot water ($80^\circ\text{C} \sim 100^\circ\text{C}$) [14,16]. Therefore, this hydrothermal sealing method possesses the advantages of

facile operation and high efficiency. On the other hand, there also exist some demerits including high energy consumption, a long time for hole sealing, degraded film hardness, high sealing temperature, uncomfortableness for operators, and corrosions as caused by volatilized water vapor [17]. Sealing by using nickel salt solutions can effectively improve the sealing quality, lower the sealing temperature, reduce the sealing time, and stabilize the organic dye molecules in the micropores of the anodic oxidation film, but the insurmountable problem lies in the environmental pollution as caused by nickel ions [18]. Additionally, sealing with a bichromate solution has the merits of easy operation and satisfactory corrosion resistance, which can thus be applied for protection applications through sealing the holes of the anodic aluminum oxide (AAO) film on aluminum alloys, but the high toxicity of hexavalent chromium, even with a carcinogenic effect, largely limits the practical applications [13].

Nanotitania has been regarded as the most promising semiconductor catalyst and environmentally friendly photocatalytic material, owing to its impressive photocatalysis, hydrophilicity, high electron-hole counter potential, and good physiochemical stability, low cost, non-toxicity and ready availability [19-24]. As a consequence, nanotitania has been extensively explored across various scientific disciplines [21,22,25-41]. For instance, nanotitania can be used to seal aluminum oxide for corrosion resistance and UV-protection by virtue of the commonly-known physiochemical stability and UV-shielding performance of the nanotitania [42,43]. However, it remains a great challenge to use nanotitania as a hole sealing material for AAO film [23-34] This study aims to grow a layer of nanotitania film for the purpose of sealing the holes of the AAO film on the aluminum alloy.

A large number of methods have been employed to prepare the titania film primarily based on the vapor phase, liquid phase, sol-gel, precipitation, and electrical deposition [21,22,25-43]. In this study, an anodic oxidation method was adopted for deposition of nanotitania under alternating voltage conditions, leading to the generation of a composite film. Our method has the following advantages: (i) due to the electrical deposition proceeded in a solution at a low temperature, no remaining thermal stress exists within the composite film, resulting in enhanced adhesion interactions between the substrate and composite film, (ii) because of the linear process of the electrical deposition, the film can be uniformly grown on the aluminum oxide matrix, with complex shape and porous surface, for hole sealing, and (iii) by means of modulating current, voltage, and pH, temperature and concentration of the solution, the thickness, chemical composition and porosity can be finely controlled, and (iv) low invest for setting the electrical deposition equipment, high utilization efficiency of raw materials, low cost during the production, ease of manufacturing, and facile operation. Therefore, such a technique holds a great promise for widespread applications. In addition, the electrical deposition approach exhibits cost-effective and simple to manufacturing characteristics, which takes only a short time to load a large amount of titania on the aluminum alloy in one cycle, outperforming the multiple coating process of sol-gel

techniques and hence showing more promising applications of coating titania on the iron and steel surface. Consequently, broad prospects of practical applications can be expected.

Materials and Methods

Aluminum oxide preparation

An aluminum alloy (6063) plate with a size of $75 \text{ mm}^2 \times 50 \text{ mm}^2$ was cleaned by ultrasonication with a small amount of detergent for 3 min to 5 min, so as to remove the oily contaminants from the plate surface. Afterwards, deionized (DI) water was used to thoroughly wash the plate, followed by washing with an alkaline solution for 3 min to 5 min and then with DI water. After these washings, the plate was placed into the pre-prepared polishing solution for 2 min to 3 min of polishing treatment, followed by thoroughly washing. After that, the plate was put into an electrolytic cell with a sulfuric acid electrolyte (17%). The aluminium alloy and lead plates were used as anode and cathode respectively, with a distance of approximately 20 cm. The oxidation processing was then carried out at a stable voltage of 3.7 V for 2000 s.

Hole sealing by two types of titanium sources

Selecting titanium potassium oxalate and ammonium hexafluorotitanate as the precursor of nanotitania is by considering their higher stability in aqueous electrolytes as compared to other kinds of precursors such as Tetraisopropyl Titanate (TIPT) and TiCl_4 due to the ready hydrolysis properties of TIPT and TiCl_4 [44,45].

The hole sealing achieved by titanium potassium oxalate-based electrical deposition is described as follows: a pre-prepared solution containing titanium potassium oxalate with a concentration of 0.01 mol/L, 0.05 mol/L or 0.1 mol/L was adopted as the electrical deposition liquid. After anodic oxidation, the aluminum alloy was dipped into the mixed electrical deposition liquid for 900 s. Upon connection of the circuit, the aluminum alloy and lead plates became the cathode and anode, respectively. The alternating voltage was set to be 3 V, 3.5 V or 4 V, with the deposition time as 300 s, 900 s or 1800 s. The optimized parameters were obtained by weight loss experiments on the samples being prepared under the conditions of different concentrations of deposition liquid, voltages, and time.

The procedures for the hole sealing by ammonium hexafluorotitanate-based electrical deposition was given below. The pre-prepared ammonium hexafluorotitanate solutions with concentrations of 0.01 mol/L, 0.05 mol/L, 0.1 mol/L were used as the electrical deposition liquid. The anodically oxidized aluminum alloy was dipped into the prepared electrical deposition liquid for 900 s. After the circuit connection, the aluminum alloy and lead plates were employed as the cathode and anode respectively. The alternating voltage was to be 3, 3.5, and 4 V, with the deposition time as 300 s, 900 s or 1800 s. The optimized parameters were found out by weight loss experiments on the samples being prepared under conditions of different concentrations of deposition liquid, voltages, and time.

Electrochemical measurements of the samples after the hole sealing:

Potential scan in 3.5% NaCl acidic (pH 2.0), neutral (pH 7.0), and alkaline (pH 12) environments was performed for the samples prepared under optimized conditions in the weight loss experiment. The scanning range, speed and testing time were set as -1.5 V~1.5 V, 20.0 mV/s, and 5 min, respectively. The electrochemical polarization curves were obtained on an electrochemical workstation (CS-310, Wuhan Branch, Instrument Co., Ltd.) using a three-electrode system. Pt and saturated calomel electrodes were used as the counter and reference electrodes, respectively. The exposure area of the specimen was 5.7 cm², with the other location sealed by epoxy. According to the above optimized result, AC impedance measurement was performed on the optimized sample. The parameters used for the measurement were given as follows:

- (i) field grounding mode;
- (ii) testing frequency range of 10⁻² Hz~10⁵ Hz;
- (iii) AC amplitude of sine wave of 10 mV;
- (iv) 470 pF and 2.2 nF broad band responses at the frequencies of >10 and <10, respectively; and
- (v) filter set as 470 nF.

The fitting processing of the obtained AC impedance data was performed by a ZView impedance analysis software, and then by an Origin software to convert the data to figures.

Results and Discussion

Weight loss experiments on the system hole-sealed by using two types of titanium sources as the precursor of nanotitania

For the same deposition liquid formulation used for hole sealing, the parameters of time, voltage, and concentration become important parameters (**Tables 1 and 2**). Through the comparison of the weight loss testing data (the weight loss of smaller than 30 mg/mm² can be considered to be qualified), it can be noted that the weight loss for hole sealing is increased with increasing the voltage. The longer the time, the lower the weight loss for hole sealing. In addition, increasing concentration lowers the weight loss for hole sealing. On the other hand, for the titanium potassium oxalate as the hole sealing liquid, the weight loss is initially increased and then decreased, with increasing the concentration. Concerning the ammonium fluorotitanate as the hole sealing liquid, the sample 8 presents a minimum weight loss of 3.2 mg/mm², while the minimum weight loss become 8.3 mg/mm² for the sample 6 in the case of the titanium potassium oxalate as the hole sealing liquid. The lower weight loss for hole sealing indicates the higher corrosion resistance and hence the better hole sealing effect. As a consequence, the optimized conditions for electrical deposition of titania are presented in the following **Table 3**.

Table 1 The weight loss results of titanium potassium oxalate-based electrodeposition of nanotitania as a function of deposition conditions including the concentration, time and voltage.

Parameter Testing No.	A Conc./mol/L	B Time/s	C Voltage/V	Weight loss Δm/(mg/mm ²)
1	0.01	300	3	11.2
2	0.01	900	3.5	35.3
3	0.01	1800	4	26.2
4	0.05	300	3.5	19.2
5	0.05	900	4	45.3
6	0.05	1800	3	8.3
7	0.1	300	4	57.5
8	0.1	900	3	24.1
9	0.1	1800	3.5	38.4

Table 2 The weight loss results of ammonium fluoride titanate-based electrodeposition of nanotitania as a function of deposition conditions including the concentration, time and voltage.

Parameter Testing No.	A Conc./mol/L	B Time/s	C Voltage/V	Weight loss Δm/(mg/mm ²)
1	0.01	300	3	18.4
2	0.01	900	3.5	44.8
3	0.01	1800	4	63.9
4	0.05	300	3.5	21.7
5	0.05	900	4	19.3
6	0.05	1800	3	9.7
7	0.1	300	4	14.6
8	0.1	900	3	3.2
9	0.1	1800	3.5	6.4

Table 3 Optimization of the conditions for electrodeposition of titanium dioxide.

Manufacturing condition	Parameter
Deposition voltage	3.0V
Conc. (ammonium fluorotitanate)	0.10mol/L
Conc. (titanium potassium oxalate)	0.05mol/L
Deposition time (ammonium fluorotitanate)	900s
Deposition time (titanium potassium oxalate)	1800s

Polarization curve measurements for the two types of titanium sources-sealed systems:

Based on the above-optimized results as obtained from weight loss experiments, the experimental conditions are given as follows:

- (i) Deposition voltage of 3 V;
- (ii) Concentration of ammonium fluorotitanate of 0.10 mol/L;
- (iii) Deposition time of 900 s;
- (iv) Concentration of titanium potassium oxalate of 0.05 mol/L; and
- (v) Deposition time of 1800 s.

Under the above-detailed conditions, polarization curves are measured. As for the system with the 3.5% NaCl solution (pH 2.0), CS-310 electrochemical workstation was adopted for the obtaining the polarization curve, with the scanning range of the anodic polarization curve of -1.5 V~1.5 V, scanning speed of 20.0 mV/s, and detection period of 5 min. The resulting polar curves are presented in **Figure 1**.

Concerning the system with the 3.5% NaCl solution (pH 2.0), self-corrosion potential for hole sealing by ammonium fluorotitanate is higher than that by titanium potassium oxalate, revealing the lower tendency of corrosion (**Table 4**). The latter exhibits a higher self-corrosion current density as compared to the former, which also indicates a higher corrosion speed leading to easier corrosion. The value of polar resistance can be calculated according to the polar resistance equations. The higher the polar resistance, the higher the quality of the hole sealing. The corrosion becomes more difficult to take place. These results can give us a conclusion that the AAO film (as sealed using ammonium fluorotitanate as the titanium source) exhibits higher corrosion resistance as compared to the one sealed with titanium potassium oxalate as the titanium source.

As for the system with the 3.5% NaCl solution (pH 7), CS-310 electrochemical workstation was used to measure the polar curves, with the electrokinetic potential scanning range of -1.5 V~1.5 V, speed of 20.0 mV/s and time of 5 min. The obtained polar curves are presented in the following **Figure 2**.

In the 3.5% NaCl solution system, the AAO film with the holes sealed with the titanium potassium oxalate as the sealing precursor shows a higher self-corrosion potential than the ammonium fluorotitanate-sealed one, meaning the higher tendency of corrosion (**Table 5**). The former shows a higher self-corrosion current density as compared to the latter, also

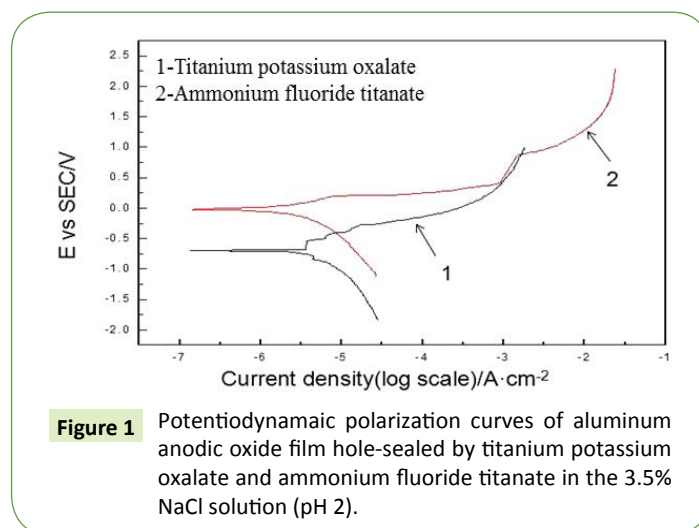


Figure 1 Potentiodynamic polarization curves of aluminum anodic oxide film hole-sealed by titanium potassium oxalate and ammonium fluoride titanate in the 3.5% NaCl solution (pH 2).

indicating the easier corrosion with a higher corrosion speed. According to the polar resistance Eq., the polar resistance can be calculated. The larger the polar resistance, the better the quality of the AAO film with the holes sealed. The smaller tendency of corrosion can thus be achieved.

In the 3.5% NaCl solution system (pH 12), CS-310 electrochemical workstation was used to measure the polar curves, with the electrokinetic potential scanning range of -1.5 V~1.5 V, speed of 20.0 mV/s and time of 5 min. The obtained polar curves are presented in the following **Figure 3**.

In the system with a 3.5% NaCl solution (pH 12), the AAO film with the holes sealed using ammonium fluorotitanate as the precursor shows an apparently lower self-corrosion potential as compared to the titanium potassium oxalate-sealed one, indicating a lower tendency of corrosion (**Table 6**). The latter also exhibits a higher self-corrosion current density, also revealing a higher corrosion speed and hence easier corrosion. The polar resistance can be calculated according to the polarization resistance equations. The larger value of polar resistance indicates the higher quality of the sealed film and hence higher resistance to the corrosion.

From the results presented in **Figures 1- 3**, it can be noted that, for all the systems with the NaCl solution under acidic to alkaline conditions, AAO film sealed with ammonium fluorotitanate as the precursor shows lower self-corrosion potentials as compared to the titanium potassium oxalate-sealed one, thus indicating their lower corrosion speeds. The polar resistance as calculated from the polar resistance equations also reveals the higher quality of the sealed AAO film using ammonium fluorotitanate

Table 4 Electrochemical parameters adopted for obtaining potentiodynamic polarization curves at pH 2.

pH=2.0	Electrochemical parameter				Polarization resistance/ Ω
	E_{corr}/V	I_{corr}/A	B_c/mV	B_a/mV	
Ammonium fluorotitanate system	-0.1673	1.1825×10^{-7}	488.3	1186	3.047×10^6
Titanium potassium oxalate system	-0.5566	1.0771×10^{-6}	388.6	600	4.446×10^5

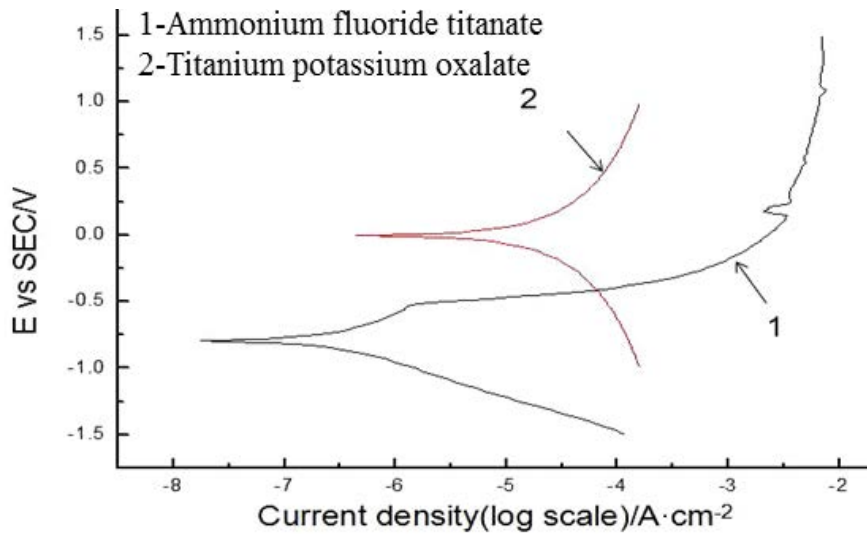


Figure 2 Potentiodynamic polarization curves of aluminum anodic oxide film hole-sealed by titanium potassium oxalate and ammonium fluoride titanate in the 3.5% NaCl solution (pH 7).

Table 5 Electrochemical parameters of potentiodynamic polarization curves at pH 7.

pH=7.0	Electrochemical parameter				Polar resistance/ Ω
	E_{corr}/V	I_{corr}/A	B_c/mV	B_a/mV	
Ammonium fluorotitanate system	-0.9332	5.1786×10^{-6}	222.1	359.08	4.8659×10^6
Titanium potassium oxalate system	-0.0202	9.7656×10^{-6}	614.9	659.3	4.0516×10^6

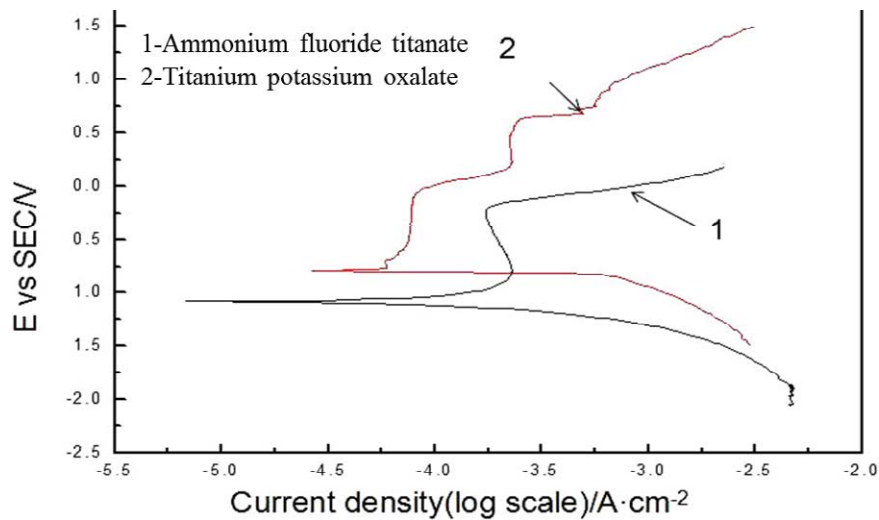


Figure 3 Potentiodynamic polarization curves of aluminum anodic oxide film with titanium potassium oxalate and ammonium fluoride titanate for hole sealing in a 3.5% NaCl solution at pH 12.

Table 6 Electrochemical parameters of Potentiodynamic polarization curves at pH 12.

pH=12	Electrochemical parameter				Polarization Resistance/ Ω
	E_{corr}/V	I_{corr}/A	B_c/mV	B_a/mV	
Ammonium fluorotitanate system	-0.7385	6.60093×10^{-4}	513.3	770.6	1.9874×10^3
Titanium potassium oxalate system	-0.1.086	2.4595×10^{-7}	649.4	1245.8	1.7907×10^7

as the precursor. These findings can be attributed to the stronger chemical bonding between Al_2O_3 and TiO_2 as formed by AC deposition with ammonium fluorotitanate. Moreover, the layers of the film are more compact and stable.

AC impedance measurements for the system hole-sealed by two types of titanium sources

On the basis of the above optimized results, it can be found that the best hole sealing effect can be achieved at 3 V; consequently, the samples sealed at 3 V (using both ammonium fluorotitanate and titanium potassium oxalate as the precursor) were used to conduct the impedance measurements, with the results shown in **Figure 4**.

Under the same conditions, the electrochemical impedance spectra are captured for the ammonium fluorotitanate- and titanium potassium oxalate-sealed samples at 3 V. Based on the analysis results of the electrochemical impedance spectra, the larger the radius of capacity reactance arc, the higher is the impedance, along with a higher resistance and hence a higher corrosion resistance (**Figure 4**). It can also be found that the radius of the impedance pattern for ammonium fluorotitanate-sealed sample is obviously larger than that for titanium potassium oxalate-sealed sample, which is an indication of the more compact and stable AAO film with the holes sealed using ammonium fluorotitanate as the precursor, together with higher impedance. This results in the higher corrosion resistance as compared to the titanium potassium oxalate-sealed sample.

Conclusion

By virtue of the weight loss experiment, this study has demonstrated that the minimum value of weight loss reaches 3.2 mg/mm^2 as for the system sealed by the nanotitania using ammonium fluorotitanate as the precursor for electrical deposition-based hole sealing, while the corresponding minimum value is as high as 8.3 mg/mm^2 as for the system involving titanium potassium oxalate. Both the titanium sources can contribute to the hole sealing and meet with the demand for corrosion resistance of the anodic aluminum oxide. More compact TiO_2 film are formed on the surface of the aluminum

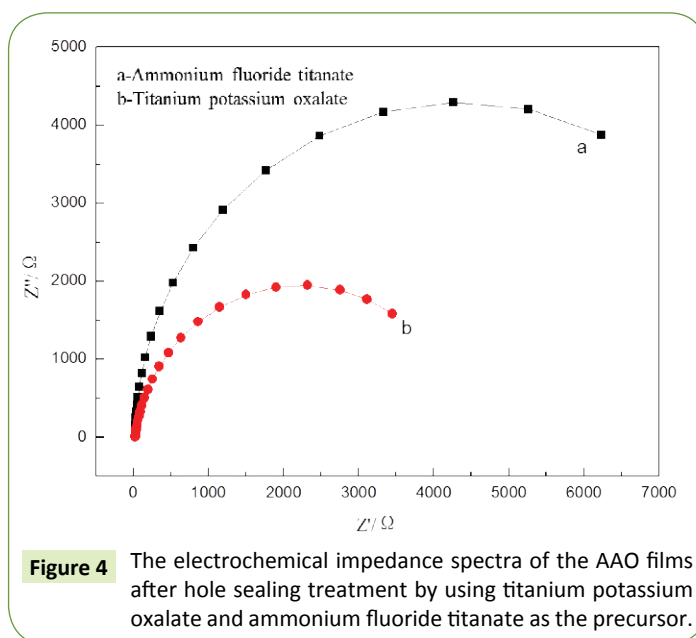


Figure 4 The electrochemical impedance spectra of the AAO films after hole sealing treatment by using titanium potassium oxalate and ammonium fluoride titanate as the precursor.

alloy as sealed by the nanotitania with ammonium fluorotitanate as the precursor, as indicated by the potential scanning and AC impedance measurements after the optimization from the weight loss experiment. This contributes to the higher stability and corrosion resistance as compared to the titanium potassium oxalate-sealed one under all the pH conditions considered in this study. The optimal condition for hole sealing is demonstrated to be ammonium fluorotitanate of 0.1 mol/L, AC voltage of 3 V, and deposition time of 900 s.

Acknowledgements

We greatly appreciate the Engineering Project for Innovating and for Enhancing Universities of Guangdong Province (2016GCZX008), Natural Science Foundation of China (21671038), the Project Funded by Engineering Technology Center of Foshan City (2014GA000355), the Special Funds for Innovation of Science and Technology of Foshan City (2014AG10009), and the Key Platform Financing Programs from the Education Department of Guangdong Province (gg041002).

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