

Electrochemical Characterization of Titanium Oxide Nanotubes Fabricated by Anodizing in Three Kinds of Electrolytes

A. A. Al-Swayih

Department of Chemistry, College of Science, Princess Nora Bint Abdul Rahman University
aswayih@yahoo.com

Abstract: The present paper is focused on comparative behavior of various nanotubes growth on titanium using electrochemical procedure. The anodizing method under controlled conditions was performed in three kinds of electrolytes as following: a mixture of fluoride salts as inorganic solution (1M $(\text{NH}_4)_2\text{SO}_4$ + 0.5 wt.% NH_4F), and an organic solution as Glycerol + NH_4F (0.5 wt.%), and a mixture of glycerol and water (1:1 vol.%) + 0.5 wt.% NH_4F . The obtained surface nanostructures were investigated with a Scanning Electron Microscope, open circuit potential, Tafel plots and Electrochemical impedance spectroscopy. As a conclusion the titanium oxide nanotubes obtained in hybrid organic + inorganic components as glycerol-water (1:1 vol.%) + 0.5 wt.% NH_4F leads to more performances. The presence of glycerol with water in the electrolyte can facilitate the formation of well-ordered TiO_2 nanotubes. This is not observed in organic electrolyte, because the glycerol causing a greater ohmic potential drops, and the high viscosity of glycerol can suppress the formation of nanotube structure.

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1. Introduction:

In the past decades, nanoscale structures of TiO_2 have attracted increasing scientific and technological attention due to the increased exploitation of the specific functional properties of TiO_2 in applications [1].

For instance, the nanotubes show a high photoresponse, when annealed [2], they show extremely high sensitivity to hydrogen when used as gas-sensor [3], they can extremely change their surface wettability [4,5], they can act as a catalyst support for methanol electro oxidation [6], or they can be N-doped by annealing in NH_3 [7] or by N-ion implantation [8,9]. Additionally, they can serve as a very suitable substrate for hydroxyapatite growth in biomedical application [1,10].

Titanium oxide nanotubes can be prepared by various techniques such as sol-gel method [11], electrophoretic deposition [12] and anodization [13-16]. Anodization is preferred to the sol-gel or electrophoretic methods, as it provides strong adherent TiO_2 layer than the latter two methods [17].

Anodization is recognized as a self-ordering electrochemistry approach to form some nanoscale structures [18]. In 1999, Zwilling *et al.* [19] were the first to obtain self-ordered TiO_2 nanostructures by anodizing Ti in a fluoride containing electrolyte. In 2001, Gong *et al.* [20] fabricated well aligned and organized TiO_2 nanotubes by anodization of a pure titanium sheet in an aqueous HF electrolyte.

The tubes length of TiO_2 nanotubes grown in HF containing acid electrolytes did not exceed 500nm [21,22]. Longer nanotubes were produced using

neutral fluoride instead of the acid electrolytes [13,23]. Acidic or neutral electrolytes invariably produced rippled tubular structures. The efficiency of this process (using acidic or neutral fluorides) is less than 40%. Usage of organic electrolytes containing fluoride ions is shown to produce long length and smooth TiO_2 nanotubes [24]. Specifically, in glycerol containing fluoride electrolytes, the nanotubes have an aspect ratio reaching up to about 150 and current efficiency for nanotube formation is close to 100% [1], and glycerol containing electrolytes are better than the ethylene glycol based ones [25].

The previous experiments on the effect of various nanotubes structure indicated that electrochemical stability, ion release, cell behavior are favourably modulated and significantly different as a function of conditions of nanotubes formation, in particular for the nanotubes obtained in hybrid electrolyte with an organic part, which as expected may act and reacts more friendly with protein and other organic components [26].

Further progress was recently achieved by using a viscous electrolyte containing fluoride ions. Prior experiments showed that nanotubes with very smooth tube walls and length of several micrometers can be achieved [24].

The objective of the research described here is a comparative behavior of nanotubes growth on titanium using anodizing in three kinds of electrolytes: the first is a mixture of fluoride salts in water for inorganic solution (1M $(\text{NH}_4)_2\text{SO}_4$ + 0.5 wt.% NH_4F), and the second is a hybrid inorganic + organic components as glycerol + 0.5 wt % NH_4F . These two

kinds of electrolytes are representative of anodic growth of self-organized TiO₂ nanotubes in water-based electrolytes and in viscous electrolytes [24,27–30]. The third solution is a mixture of water and glycerol (1:1) containing the same amount of fluoride salts. Lai *et al.* [31] and Macak *et al.* [1] found that the optimized volumetric ratio of glycerol vs. deionized water needed to efficiently fabricate nanotube array layer was between 1:1 and 2:1.

2. Material and methods

2.1. Titanium oxide nanotube layer formation

Ti foils with an area of 20 mm x 30 mm and thickness of 0.25 mm (99.5% metal basis, Alfa Aesar) were used as starting material in order to obtain the titanium oxide (TiO₂) nanotube arrays. A preliminary treatment was performed by degreasing the titanium foils using sonication in acetone, in isopropanol, and, finally, in methanol. The foils were subsequently rinsed with deionized water and dried in a nitrogen stream. Titanium oxide nanotube arrays were formed by anodization in three types of solution: 1M (NH₄)₂SO₄ + 0.5 wt.% NH₄F in water (sample A), mixture of glycerol and water (50:50 vol.%) + 0.5 wt.% NH₄F (sample B) and Glycerol + NH₄F (0.5 wt.%) (sample C). Table 1 summarizes the samples used in this study.

These electrolytes were selected in order to explore the influence of electrolyte kind (organic, inorganic or hybrid) on the tube growth while keeping the amount of F⁻ species constant. Based on our previous experience, we decided to use applied potential of 20V for 30 min [32].

Initially anodization was done by ramping up to the specific end potential with a ramping speed of 1 V s⁻¹ and holding it for 30 min at room temperature. Following the anodization, the samples were rinsed with deionized water and dried in a nitrogen stream.

2.2. Surface characterization

The surface morphology of the titanium oxide nanotube arrays was characterized using a scanning electron microscope (Jeol JSM-7600F Field-Emission Scanning Electron Microscope).

2.3. Electrochemical tests

All electrochemical measurements were performed in Hank's physiological solution, which was prepared according to an earlier report [33]. In brief, the solution was prepared using the following chemicals viz., NaCl (8.00g), KCl (0.40g), CaCl₂ (0.19g), NaHCO₃ (0.35 g), Na₂HPO₄ (0.06 g), MgCl₂·6H₂O (0.19g), MgSO₄·7H₂O (0.06 g) and Glucose (1.00g). All the chemicals were dissolved in that order in 1000 mL double distilled water, the temperature and pH were maintained at 37 °C and 7.8, respectively.

A conventional three-electrode electrochemical cell system was used. Saturated calomel electrode (SCE) and platinum mesh were used as reference and counter electrodes, respectively. Potentials in the text refer to the SCE scale.

In the experiments, the open circuit potential (E_{OCP}) was measured for an hour. Then, electrochemical impedance spectroscopy (EIS) was recorded. The frequency ranged from 100 kHz to 10 mHz at 10 cycles per decade, with an ac amplitude of ±10 mV. The absolute impedance and phase angle were measured at each frequency. The impedance data were interpreted on the basis of equivalent electrical circuits, using the Zsim program for fitting the experimental data. In Tafel plots tests, the working electrode potential is continuously increased from -0.250 to 0.500 V relative to the E_{OCP} at a scan rate of 1 mV/s.

3. Results:

3.1 Surface morphology

Fig. 1 shows scanning electron microscope (SEM) images of the structures obtained after the anodization experiments. It can clearly be seen that anodization in all investigated electrolytes leads to the formation of self-organized titanium oxide nanotubes, but the resulting structures are significantly different, most importantly, the length and the diameter of the tubes differs strongly. For sample (A), the diameter of nanotubes is about 75 nm and the length is more than 830 nm. For sample (B) they are about 46 nm and 725 nm respectively. However, for the sample (C), the diameter is about 22 nm and the length is about 200 nm after 30 min of anodization.

Evidently, in this case the longest tubes are obtained in the water-based (NH₄)₂SO₄/NH₄F electrolyte. In spite of their length, however, in the water-based case the side-walls of the tubes are rough, i.e. there are ripples present. In contrast, in the pure glycerol/NH₄F mixture the tubes have very smooth walls and smaller diameter, but the surface was incompletely covered by the nanotubes structure. This is in line with previous work, where it was deduced that this wall smoothness originates from damping local spikes in the flux of reaction species within the tubes when using highly viscous electrolytes [1,24].

3.2 electrochemical measurements

3.2.1. Open circuit potential (OCP) measurements

Fig. 2 presents the variation of open circuit potential for three anodized titanium samples for one hour immersion in Hank's solution. According to this potential evolution, at the initial moment the high electronegative potential value corresponds to the (B) and (C) /Hank solution interface, followed by the value obtained for sample (A). At short immersion

time, open circuit potential (E_{OCP}) for all electrodes is shifted to more electronegative values.

After one hour immersion time, the potential tends to stabilize at more electronegative values than those corresponding to initial immersion time. For titanium nanotube samples, the oxide layer obtained exhibits nanotubes with the pores diameter depending

on electrolyte solution, but in any case more significant. The corrosion resistance increases with the decrease of oxide layer porosity, because the electrolyte penetrates pores and corrodes the metal surface. The most stable structure in this approach is the nanotube obtained in sample (B). This result is in agreement with Mindroui *et al.* results [26].

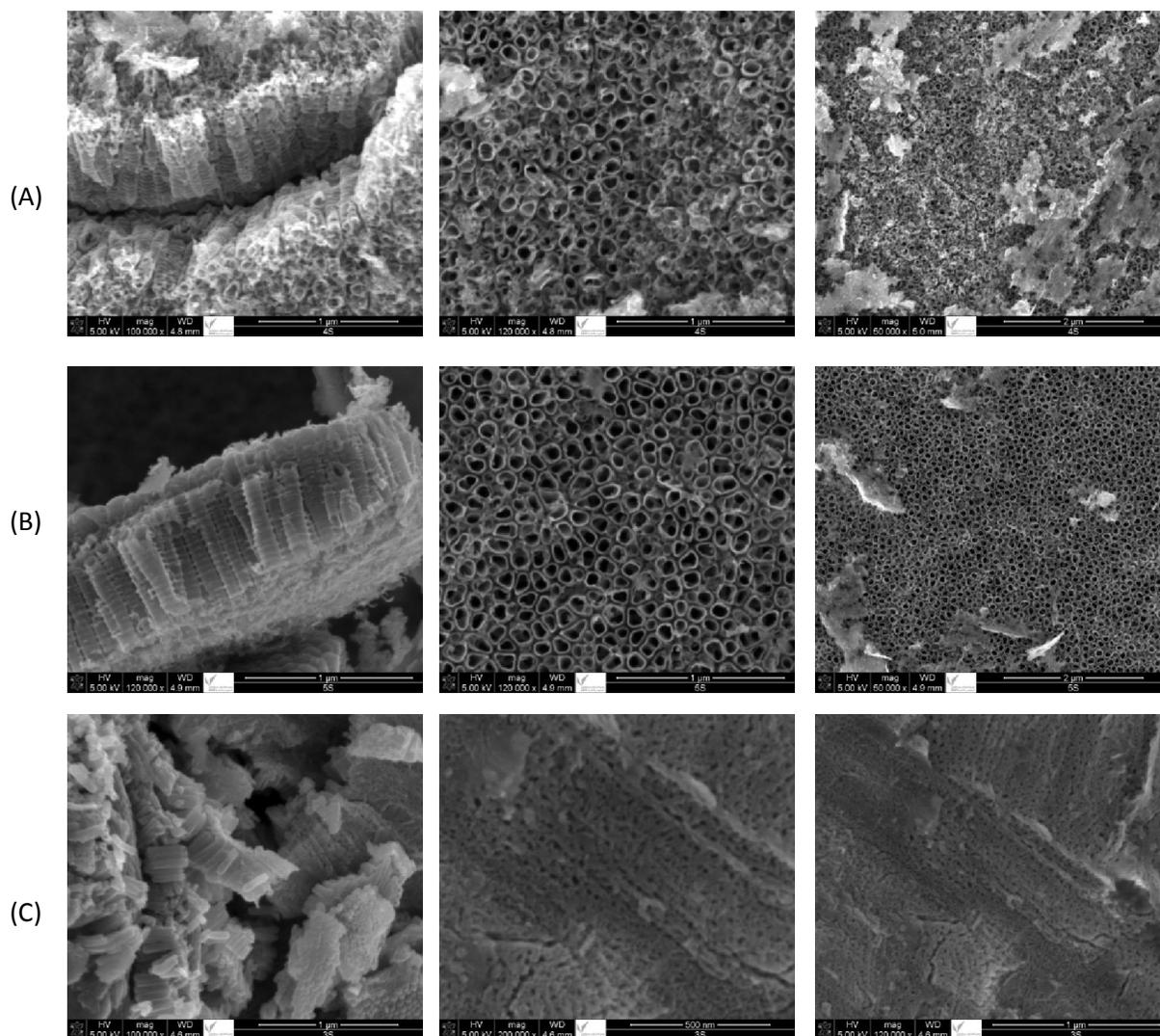


Fig. 1: The SEM images of titanium oxide nanotubes formed in different solutions.

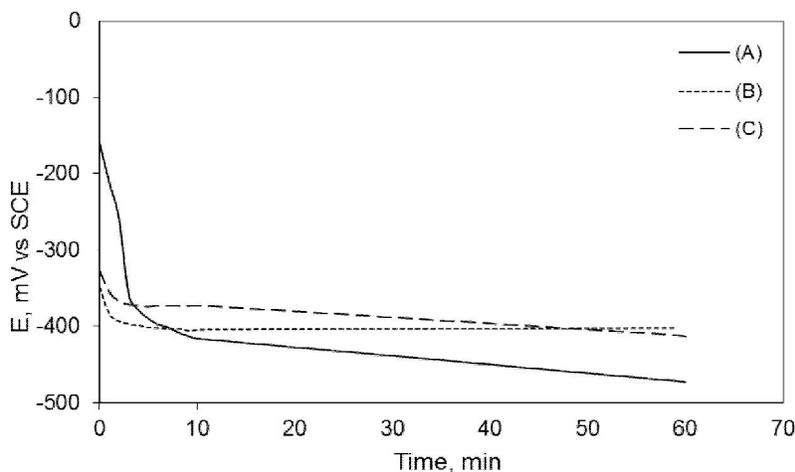


Fig. 2: The E_{OCP} of titanium oxide nanotube samples anodized in different solutions in Hank's solution

3.2.2. Tafel plots

The Tafel plots obtained after one hour immersion time in Hank's solution for titanium nanotube electrodes are presented in Fig. 3. The results of corrosion potential (E_{corr}) and corrosion current density (I_{corr}) from Tafel curves are given in Table 2.

From these results we can observe that the oxide nanotube layer anodized in a mixture of water and glycerol (sample B) has the best corrosion behavior, the current density value being smaller than those corresponding to sample (A) and (C).

3.2.3. Electrochemical impedance spectroscopy (EIS)

The processes at Ti/oxide nanotube layer interface were discussed in terms of EIS measurements according to Nyquist diagrams presented in Fig. 4. The EIS results indicated that the TiO_2 nanotube surface is composed of a bi-layered oxide consisting of an inner barrier layer associated to high impedance and responsible for corrosion protection, and an outer porous layer (nanotubes) of lower impedance. Fig. 5 shows representation of equivalent electric circuit used in fitting Nyquist spectra for anodized Titanium samples.

The equivalent circuit for titanium oxide nanotube can be presented by using two time constants [34,35], $R_s(R1Q1(R2Q2))$, where R_s corresponds to the resistance of the solution, $R1$ to the resistance of the porous layer, $R2$ to the resistance of the barrier layer, $Q1$ to the capacitance of the porous layer and $Q2$ to the capacitance of the barrier. A constant-phase element representing a shift from the ideal capacitor was used instead of the capacitance

itself, for simplicity. The impedance of a phase element is defined as $Z_{CPE} = [C(j\omega)\alpha]^{-1}$, where $-1 \leq \alpha \leq 1$. The value of α is associated with the non-uniform distribution of current as a result of roughness and surface defects layer.

The results of the fitting process are presented in Table 3. The values of $R2$ indicate that the sample B has the highest corrosion resistance. Therefore, the barrier layer formed during anodizing process in mixture of glycerol and water (1:1 vol.%) + 0.5 wt.% NH_4F solution provides more effective corrosion protection, as shown by the lower corrosion current density in table 2.

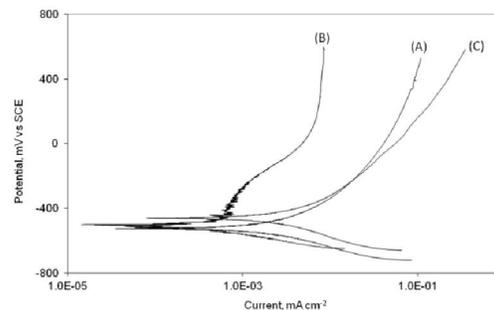


Fig. 3: Potentiodynamic polarization plots of titanium oxide nanotube samples anodized in different solutions in Hank's solution

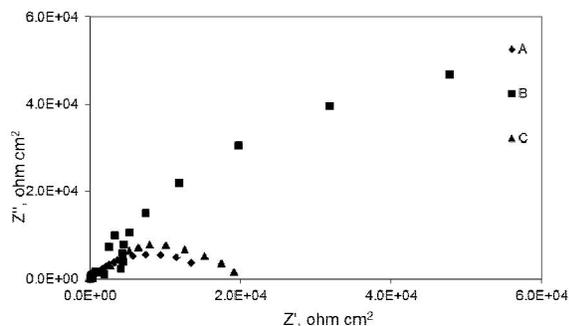


Fig.4: Nyquist diagrams of titanium oxide nanotube samples anodized in different solutions in Hank's solution

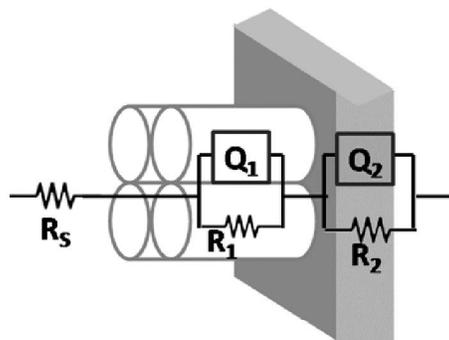


Fig. 5: Equivalent circuit used to model impedance spectra of titanium oxide nanotube

Table 1: Summary of the conditions of anodization

Sample	Electrolyte composition in anodization	voltage	time
A	1M (NH ₄) ₂ SO ₄ + 0.5 wt.% NH ₄ F	20 V	30 min
B	mixture of glycerol and water (1:1 vol.%) + 0.5 wt.% NH ₄ F		
C	Glycerol + NH ₄ F (0.5 wt.%)		

Table 2: Electrochemical parameters obtained from Tafel plots

Sample	E _{corr} V	B _a mV dec ⁻¹	B _c mV dec ⁻¹	I _{corr} x 10 ⁻³ mA cm ⁻²
A	-0.524	213	142	1.62
B	-0.498	195	99	0.28
C	-0.484	178	189	1.17

Table 3: Fitted electrochemical parameters determined from Nyquist diagrams based on the equivalent circuit presented in fig. 4

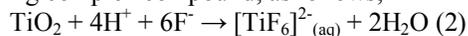
Sample	R _s ohm cm ²	R ₁ x 10 ³ ohm cm ²	Q ₁ x 10 ⁻⁴ F cm ⁻²	n ₁	R ₂ x 10 ³ ohm cm ²	Q ₂ x 10 ⁻⁴ F cm ⁻²	n ₂
A	121.5	2.41	6.01	0.91	15.3	4.40	0.87
B	96.7	14.8	2.62	0.93	131	1.07	0.88
C	135.0	6.24	2.39	0.92	17.4	2.61	0.85

4. Discussion:

When electrochemical anodization process is applied on the titanium electrode, it conducted in two stages. In the first stage the potential ramped from 0 to 30 V with a scan rate of 1 V/s. This was found to help building a barrier TiO₂ layer. The second stage of the anodization involves a potential hold of titanium at 30 V for almost 30 min. In the first stage, the formation of the high resistant TiO₂ film occur according to the following equation [36],



Under sufficient high potential the electric field will be strong enough to take the Ti⁴⁺ ions off the surface leaving behind some voids in the interpore areas [37]. Fluoride ions are able to dissolve the TiO₂ forming complex compound, as follows;



The driving force for reaction (2) is high as judged from a comparison of the standard free energies of formation of -820 and -2180 kJ/mol for TiO₂ and [TiF₆]²⁻_(aq), respectively [38].

The key reactions responsible for the formation of anodic nanoporous Al₂O₃ [19,39] and TiO₂ [19,41] apparently are similar. Initially, oxide grows at metal surface due to interaction of metal with O²⁻ or OH⁻ ions [42]. Then these anions, as the oxide thickens, need to diffuse through to reach the metal surface. At the same time Ti⁴⁺ ions diffuse out to the oxide electrolyte interface and this is facilitated by strong electric field. Simultaneously, field assisted dissolution of oxide at oxide/electrolyte interface takes place [42]. Due to high electric field the Ti-O bond undergoes polarization and is weakened promoting dissolution of the metal ions. Chemical dissolution of TiO₂ by fluoride (Eq. (2)) takes place. The rate of oxide growth at the metal/oxide interface and the rate of oxide dissolution at the pore-bottom/electrolyte interface reach equilibrium. Thereafter, the thickness of the barrier layer remains unchanged although it moves further into the metal making the pore/tube deeper.

At smaller amount of F⁻ related to higher solubility of fluoride in water (the case of aqueous electrolytes) a tendency to chemical dissolution is taking place followed by transition from pores to a tubular structure [26].

The formation of oxide films in the mixed solution required more time than that in the aqueous solutions. This is attributed to the relatively slow process of electrochemical etching of titanium in the solution containing glycerol. The higher the glycerol concentration, the greater the ohmic potential drops, which results in the suppression of the electrochemical etching process [31].

In the presence of glycerol, the competition between the formation of the Ti-glycerol complex and the restriction of fluoride ion diffusion is taking place, but the formation of the Ti-glycerol complex accelerates the dissolution of the oxide layer and facilitates the formation of well-ordered TiO₂ nanotubes. Such highly viscous electrolytes containing glycerol can suppress chemical dissolution process through decreasing the diffusion constant of the F⁻ in the electrolyte, and such behavior reveals the importance of the amount of water in electrolyte, as was suggested in some studies [1,43].

In Lai *et al.* experiments [31], the optimized volumetric ratio of glycerol vs. deionized water needed to efficiently fabricate nanotube array layer was between 1:1 and 2:1. This result is similar to that reported by Macak *et al.* [1].

On the other hand, in spite of the differences in the morphology of titanium oxide nanotubes formed in organic and inorganic solution, there are little differences between the electrochemical behavior of sample A and sample C. This behavior can be attributed to the effect of the diameter and thickness of the oxide nanotubes. The larger pore diameter in the TiO₂ nanotube array introduces a larger effective exposed area in close proximity with the electrolyte thus enabling diffusion of corrosive ions in the electrolyte [45,46]. But the larger nanotubes provide more channels for the electrolyte to reach the barrier layer, consequently increasing the chance of the reaction between corrosive ions and titanium oxide [47,48].

Based on these results, both the thickness of the barrier layer and the morphology of the titanium oxide nanotubes might be influenced by the composition of the solution used in the anodization process. Thus, effect on the electrochemical corrosion behavior of TiO₂ nanotubes atop the surface of titanium foil in Hank's solution. The wall between TiO₂ nanotubes may be another important factor influencing the electrochemical stability [49].

5. Conclusion:

We have carried out a study of the electrochemical corrosion of TiO₂ nanotubes anodized in three kinds of electrolyte: inorganic, organic and hybrid one. The morphology of prepared nanotube affected by the kind of the solution employed in the anodization process, especially its diameter and thickness and the ordered of the nanotubes structure.

The TiO₂ nanotubes anodized in hybrid electrolyte (1:1 V% glycerol-water) exhibited a larger corrosion resistance indicated from corrosion current density (I_{corr}) and the value of the resistance of the barrier layer (R_2) from electrochemical impedance spectroscopy measurements.

In the mixed solution, the Ti-glycerol complex formed and restriction of fluoride ion diffusion, but it accelerates the dissolution of the oxide layer and facilitates the formation of well-ordered TiO₂ nanotubes. This is not observed in organic electrolyte, because the glycerol causing a greater ohmic potential drops, and the high viscosity of glycerol can decrease the diffusion constant of the F⁻ in the electrolyte, which results in the suppression of the chemical dissolution process, thus the surface was not completely covered by the nanotube structure.

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