Formation of Corrosion Resistant Hard Coating of LiTaO$_3$ by Anodizing in Molten LiNO$_3$

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Abstract: Background: Lithium tantalate (LiTaO$_3$) thin film was synthesized and in situ coated on tantalum substrate via anodic oxidation.

Methods: The effects of temperature, voltage and time on composition, morphology and hardness of film were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Vickers hardness, respectively.

Results: Our results showed that surface hardness of all coated samples has been increased compared with that of pure tantalum. The value of hardness was found to gradually increase with temperature, voltage and reaction time of the coating process. Selected specimens, after coating, were immersed into 10 wt% NaOH solution at 50°C for 96h to explore their anti-corrosion performance. Immersing results indicated that LiTaO$_3$ coated samples have a smaller mass loss and corrosion rate compared to those of pure Ta substrate. Pure tantalum sample and those coated by LiTaO$_3$ thin film were further examined by electrochemical methods including open-circuit potential (OCP), potentiodynamic polarization curves and electrochemical impedance spectra (EIS).

Conclusion: We have found that samples coated with LiTaO$_3$ thin film exhibit higher potentials and lower corrosion current densities than those of pure tantalum substrate, according to the results and analysis of OCP curves and potentiodynamic polarization curves. Upon anodic oxidation, samples display higher polarization resistance with higher resistance to corrosion.

Keywords: LiTaO$_3$ thin film, anodic oxidation, anticorrosion, NaOH solution, tantalum substrate, molten LiNO$_3$.

1. INTRODUCTION

Pure tantalum (Ta) and its alloys have been applied in many fields for their good biocompatibility [1-2] and corrosion resistance in a wide variety of media, especially in acids and neutral solutions [3-6]. It’s well known that their excellent anticorrosion performance is attributed to the generation of dense surface oxide film [7-8]. However, the surface hardness of pure tantalum is somehow a bit low for some applications where compaction and deformation may be an issue. Furthermore, pure tantalum cannot withstand the erosion of alkaline solutions containing NaOH [9] or KOH [10]. Therefore, method to harden the surface of pure tantalum is of great importance. Despite this need with an extensive effort being focused on surface reinforcement [11-12], to our knowledge, little [9, 13-14] was reported on the corrosion behavior of tantalum in alkaline solutions.

Lithium tantalate (LiTaO$_3$), of exceptional high hardness (5.5-6 Mohs), has received considerable attention as material choice for optoelectronic devices [15-17] in pyroelectric and piezoelectric detectors, surface acoustic wave filters, optical waveguides, optical switches and random access memories (RAM), owing to its unique piezoelectric, pyroelectric, ferroelectric, electro-optic, acousto-optic and non-linear optical properties [18-20]. Laser deposition, sol-gel method, chemical vapor deposition (CVD) and magnetron sputtering have been tried to synthesize LiTaO$_3$ film [21-24]. Note here, LiTaO$_3$ film prepared by these means may flake off easily from the substrate due to their large difference in thermal expansion coefficients (16.1×10$^{-6}$/K of LiTaO$_3$ vs. 6.6×10$^{-6}$/K of tantalum). Similar cases occurred for instance between the layer of LiTaO$_3$ and silicon (16.1×10$^{-6}$/K of LiTaO$_3$ vs. 3×10$^{-6}$/K of silicon) [25]. It is then highly desirable to search for an effective method to deal with this thermal expansion problem.

Anodic oxidation [26] seems to be a promising way worth trying. Phase diagram of Ta$_2$O$_5$ with LiOH (obtained from LiNO$_3$) also shows the appearance of LiTaO$_3$ [27], this may provide a possibility to get a good protective layer against solution erosion. As some Ta-based products tend to be used in an environment containing 10 wt% NaOH, the...
objective of present work is then to synthesize and coat LiTaO₃ thin film on tantalum substrate in situ by anodic oxidation. After coating, we will investigate the change of surface hardness and corrosion behavior of samples in NaOH solution. In comparison, composition, morphology, surface hardness and anticorrosion performance of pure tantalum and those coated by LiTaO₃ film will be examined and discussed in detail. Both traditional immersion corrosion tests and electrochemical measurements will be employed to study the performance of anticorrosion.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and Synthesis

Tantalum foil, 19 mm in diameter × 0.5 mm in thickness, was provided by Changsha South Tantalum Niobium Co., Ltd, China, with nominal chemical composition (mass fraction, %): H≤0.0015, C≤0.01, N≤0.01, O≤0.015, Si≤0.005, Fe≤0.005, Ni≤0.002, W≤0.01, Mo≤0.01, Ti≤0.002, Nb≤0.03, with Ta be balance. The apparent exposed area was 2.84 cm².

All chemicals used here are of analytical grade purchased from Sinopharm Chemical Reagent Co. Ltd. (China) without further purification. Acetone and ethanol were employed to degrease Ta foils. LiNO₃ and NaOH were used and acted as the electrolyte of anodic oxidation and solute of corrosion solution, respectively. Note here, LiNO₃ (melting point of 255°C) is a strong oxidant, can absorb water and produce derivatives such as LiOH. Water was therefore carefully removed during our processing of melting LiNO₃ (400°C to 600°C) to prevent such things from happening.

Setup of equipment for synthesizing LiTaO₃ thin film was shown in Fig. (1) schematically. Steps to synthesize and coat LiTaO₃ thin film were according to the followings:

1) Heating nickel crucible to 490°C and holding at this temperature until LiNO₃ electrolyte to be melted completely.

2) Rinsing Ta foils one after another with acetone, ethanol, distilled water, followed by drying them at 80°C for 1h.

3) Bolting cleaned Ta foils onto anode and immersing them completely in molten LiNO₃. Then apply voltage between anode and cathode by DC power for electrochemical reactions.

4) Pulling out samples at the end of coating (after going through required reactions) and cleaning them ultrasonically in distilled water, drying at 80°C in air for further tests and characterizations.

In addition, the influences of temperature, voltage and reaction time on composition, morphology and hardness of reacted thin film were investigated. Composition and surface morphology of coated samples were measured using X-ray diffraction (XRD, D/Max 2500, Rigaku, Japan) and scanning electron microscopy (SEM, Quanta-200, FEI, USA), respectively. The surface hardness of Ta substrate and LiTaO₃ thin film coated samples was measured by Vickers hardness tester (DHV, 1000) under the loading of 4.9N at dwelling time of 15s. Pure tantalum (S0) and coated samples (S1-S7) were nominated according to their synthesis parameters and listed in Table 1.

2.2. Immersion Corrosion Tests

Preliminary immersion corrosion tests were conducted to investigate anticorrosion of Ta substrate and LiTaO₃ thin film coated samples. First, accurately weighed flaky NaOH was dissolved in distilled water to prepare 10 wt% NaOH solution. Then, tantalum substrate and samples coated by LiTaO₃ thin film were immersed into as-prepared 10 wt% NaOH solution at 50°C for 96h to monitor their mass changes. During immersion testing, all samples went through repeated pulling-out, ultrasonically cleaning in distilled water, drying and weighing in air at interval of 12h. Finally, a microstructure of surface was characterized by SEM for each sample at the end of immersion test set at 96h. Besides, the corrosion rate and corrosion inhibition efficiency were calculated through Eqs. 1 and 2 [28, 29]:

\[
V_{coor} = \frac{M_{o} - M_{i}}{A_{Ta}} \quad (1)
\]

\[
IE_{coor} = \frac{\Delta M_{Ta} - \Delta M_{Coat}}{\Delta M_{Ta}} \quad (2)
\]

Where and are initial and final mass of tested sample, is apparent exposed area of the sample, is immersion time, and denote the mass losses of Ta substrate and coated samples in tested solution.
2.3. Electrochemical Measurements

Electrochemical tests were carried out in 10 wt% NaOH solution at 50°C by the workstation (ZAHNER IM6ex), in order to further study the anticorrosion performance of tantalum substrate and samples coated by LiTaO3 thin film. Platinum foil and saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. To avoid contamination, the SCE was connected via a bridge filled by 10 wt% NaOH solution with tip being pressed against the surface of working electrode to minimize IR drop. All potentials obtained in this work were referred to this reference electrode. Prior to polarization, the working electrode was immersed in testing solution for 1h to stable open-circuit potential (OCP). Upon equilibrium, potentiodynamic polarization curve was measured at scanning rate of 1 mV/s, covering from -1 to 0.5 V. Electrochemical impedance spectra (EIS) was performed using AC signal of amplitude 10 mV at pre-set potential covering frequency range of 100 kHz to 0.01 Hz. Each testing was conducted with freshly prepared solution.

3. RESULTS AND DISCUSSION

3.1. Composition Analysis

XRD spectra of samples prepared in different conditions are presented in Figs. (2) and (3). All crystalline phases observable here are lithium tantalate (LiTaO3, JCPDS No. 29-0836), tantalum pentoxide (Ta2O5, JCPDS No. 18-1304), tantalum oxide (Ta2O, JCPDS No. 74-2305) and tantalum (Ta, JCPDS No. 04-0778).

![Fig. (2). XRD spectra of samples synthesized as function of coating time.](image)

Fig. (2) shows the influence of coating time on XRD spectra for the growth of LiTaO3 thin film [XRD spectra of Ta substrate is shown in the inset of Fig. (2)]. Note, strong diffraction peaks for sample S1-1h are corresponding to Ta2O5, Ta2O and Ta (being substrate) with one weak peak of LiTaO3. Up to 3h, both peak number and intensity of LiTaO3 increased, while those of Ta2O5 and Ta2O declined (S2-3h). These become even more profoundly at 5h, with weak peaks for Ta2O3 and Ta2O (even Ta) still visible (S3-5h). That is to say, prolonged reaction will increase the content of LiTaO3 while consuming tantalum oxides. In summary, crystalline phase of LiTaO3 grows with coating time at consumption of those of Ta2O3 and Ta2O. In another word, the formation of LiTaO3 was somehow the result of a series of reactions among Li+ ions in solution with surface oxides Ta2O5 and Ta2O. These results are in agreement with those of early report [30]. The phase evolution observed here could be described as such,

Oxidation of pure Ta substrate occurred initially and spontaneously:

$$4\text{Ta} + \text{O}_2 \rightarrow 2\text{Ta}_2\text{O}_5$$  \hspace{1cm} (3)

and

$$2\text{Ta}_2\text{O}_5 + 4\text{O}_2 \rightarrow 2\text{Ta}_2\text{O}_3$$  \hspace{1cm} (4)

or

$$4\text{Ta} + 5\text{O}_2 \rightarrow 2\text{Ta}_2\text{O}_5$$  \hspace{1cm} (5)

Followed by reactions between Ta2O5 with molten LiNO3 solution:

$$2\text{Ta}_2\text{O}_5 + 4\text{LiNO}_3 \rightarrow 4\text{LiTaO}_3 + 4\text{NO} + 3\text{O}_2 \uparrow,$$

$$\Delta_rG_m(490^\circ\text{C}) = -19.3 \text{kJ/mol}$$  \hspace{1cm} (6)

or

$$2\text{Ta}_2\text{O}_5 + 4\text{LiNO}_3 \rightarrow 4\text{LiTaO}_3 + 4\text{NO}_2 \uparrow + \text{O}_2 \uparrow,$$

$$\Delta_rG_m(490^\circ\text{C}) = -19.6 \text{kJ/mol}$$  \hspace{1cm} (7)

or

$$\text{Ta}_2\text{O}_5 + 2\text{LiNO}_3 \rightarrow 2\text{LiTaO}_3 + \text{NO}_2 \uparrow + \text{NO} \uparrow + \text{O}_2 \uparrow,$$

$$\Delta_rG_m(490^\circ\text{C}) = -19.4 \text{kJ/mol}$$  \hspace{1cm} (8)

In addition, following reaction may also occur at the same time:

$$\text{Ta}_2\text{O}_3 + 2\text{LiOH} \rightarrow 2\text{LiTaO}_3 + \text{H}_2\text{O} \uparrow,$$

$$\Delta_rG_m(490^\circ\text{C}) = -30.1 \text{kJ/mol}$$  \hspace{1cm} (9)

![Fig. (3). XRD spectra of coated samples synthesized at different voltage and temperature.](image)
Note here, values of $\Delta G_m$ (Gibbs free energy change) were calculated by HSC 6.0. As $\Delta G_m$ of Eqs. (5-9) is negative, meaning these reactions can take place spontaneously. There are no $\Delta G_m$ values assigned for Eqs. (3-4) due to lack of data of $\text{Ta}_2\text{O}_5$ in HSC database. However, we were able to detect trace of $\text{Ta}_2\text{O}_5$ phase in XRD spectra, which allows us to propose such reactions for oxidation of Ta substrate to first form $\text{Ta}_2\text{O}_5$, followed by formation of $\text{Ta}_2\text{O}_3$. The difference of $\Delta G_m$ value for Eqs. (6-8) is negligible which meaning that these reactions can all take place independently to form $\text{LiTaO}_3$. It is in case there is indeed some $\text{LiOH}$ (melting point of 462°C, one possible intermediate product in our system) presented, it will also form $\text{LiTaO}_3$ by reacting with $\text{Ta}_2\text{O}_3$ (seeing Eqn. 9).

The influence of coating voltage and temperature on XRD patterns of $\text{LiTaO}_3$ thin film is presented in Fig. (3). XRD spectra of Ta substrate is shown in the inset of Fig. 3). All diffraction peaks for sample S4-5V matched well with those of $\text{Ta}_2\text{O}_5$, $\text{Ta}_2\text{O}_3$ and Ta (being substrate). Once coating voltage increased to 15V, we began to see the peaks for $\text{LiTaO}_3$, which is co-existed with those of $\text{Ta}_2\text{O}_5$ and $\text{Ta}_2\text{O}$ (S5-15V). There must be a threshold of voltage during coating, above which tantalum oxides can react with Li$^+$ to form $\text{LiTaO}_3$. That is to say, improving voltage will first accelerate the formation of tantalum oxides as an intermediate and then transformed into $\text{LiTaO}_3$ film. For sample S6-450°C, strong and sharp peaks were assigned to $\text{Ta}_2\text{O}_5$, $\text{Ta}_2\text{O}_3$ and Ta (being substrate), with one feeble peak belonging to $\text{LiTaO}_3$. Nevertheless, peak number and intensity of $\text{LiTaO}_3$ and $\text{Ta}_2\text{O}_3$ changed constantly with coating temperature up to 530°C, while those of $\text{Ta}_2\text{O}_5$ and Ta declined (S7-530°C). Comparing S6-450°C, S2-490°C, S7-530°C, we found the fact that the content of $\text{Ta}_2\text{O}_3$ was increased rapidly, accompanying with slow increase of $\text{LiTaO}_3$. These changes indicated that the effect of temperature on the formation of $\text{Ta}_2\text{O}_3$ is greater than that of $\text{LiTaO}_3$. These results may suggest that there is an optimal coating temperature range for the formation of $\text{LiTaO}_3$. Giving enough time, intermediate tantalum oxides can produce pure $\text{LiTaO}_3$ thin film theoretically. However, we found that continuously formed films retard the reaction of Li$^+$ ions and even worse, some surface began to peel off as so many hard and brittle $\text{LiTaO}_3$ particles presented there. Using our current technique, we could not get pure $\text{LiTaO}_3$ on Ta substrate. That is why the XRD spectra of $\text{LiTaO}_3$ coated samples also contained tantalum oxides. Therefore, it is very important to select reasonable experimental parameters for actual production. In this paper, the optimal preparation condition is S2 (synthesis condition is 490°C-5V-3h) and more details will be discussed in Section 3.4.

3.2. Morphology Analysis

Surface morphologies of $\text{LiTaO}_3$ thin film synthesized at different coating time are presented in Fig. (4a-c) associated with 1, 3 and 5h, respectively. In general, all samples were composed of similar coarse grains on surface with some laminar asperities. Specifically, laminar asperities were different from each other and all glowing with coating time, being small at 1 (Fig. 4a) and 3 h (Fig. 4b), and got larger at 5 h (Fig. 4c). This might due to the existence of various defects in Ta substrate, which provide different driving force (according to Yang’s equation: $\sigma_{LS} = \sigma_{ns} + \sigma_{lC}\cos\theta$) for nucleation and growth. Defects reduce energy barrier of heterogeneous nucleation which are beneficial to diffusion, aggregation, clusters coalescence and growing of coating [31]. This could explain why the size of laminar asperities coated of 5h (Fig. 4c) is much larger than those of 1 (Fig. 4a) and 3h (Fig. 4b).

Typical surface morphologies of $\text{LiTaO}_3$ thin film synthesized as function of coating voltage (Figs. 5a and 5b) and temperature (Figs. 5c and 5d) are depicted in Fig. (5). Coated sample synthesized at 5V has smooth surface accompanying with very small laminar asperities (Fig. 5a), this becomes rough with many larger laminar asperities as voltage increased to 15V (Fig. 5b). Similar morphology change has been occurred for samples coated at 450 (Fig. 5c) and 530°C (Fig. 5d). According to the classical theory of thermally induced crystallization and electrical field induced crystallization, energy exerted from external forces is proportional to temperature or voltage which affects rate of diffusion or ionic electromigration [32]. Increasing voltage or temperature will for sure provide more energy for nucleation, diffusion, merge of atoms and even worse abnormal grain growth. This is why surface morphology gets rough and coarsen for samples synthesized at higher coating voltage and temperature. Surface morphology of coatings formed at different voltage and temperature may not distinguishable, attributed to their similar influence on nucleation and growth.

![Fig. (4). SEM images of LiTaO3 film synthesized as function of coating time: (a) 1 h, (b) 3 h, (c) 5 h.](image)
To further determine coating thickness, Back Scattered Electron (BSE) images of cross-sections of coated samples were measured. Cross-section morphology (Fig. 6a) and EDS (Fig. 6b) of LiTaO\textsubscript{3} coated sample S2 are shown in Fig. (6). There is no clear boundary between substrate and coating (Fig. 6a) due to low contrast. We could not get the thickness directly from BSE images of cross-sections. Instead, the film thickness was taken from the distance of elemental distributions of tantalum and oxygen along the cross-sections (Fig. 6b). Thickness of S2 was estimated to be around 3μm. Note here, this is total thickness of mixed film containing LiTaO\textsubscript{3} and tantalum oxides, as we could not get pure LiTaO\textsubscript{3}. Samples (S1-S7) were also treated in the same way with corresponding thickness data listed in Table 2. Generally speaking, the cross-section of coating morphology of these samples is similar to the thickness proportional to voltage (S4-S5) or temperature (S6-S7).

3.3. Hardness Analysis

Vickers hardness measurement was used to study the mechanical properties of samples coated by LiTaO\textsubscript{3} thin film (Fig. 7). Note here, the hardness of Ta substrate is about 140 HV. As can be seen from Fig. (7), surface hardness of all coated samples are much higher (≥ 300 HV) and increased with coating time (Fig. 7a), voltage (Fig. 7b) and temperature (Fig. 7c) as well, due to in situ formation of increased amount hard phase of LiTaO\textsubscript{3} and tantalum oxides (see Fig. 2). For example, the content of LiTaO\textsubscript{3} in sample S7 (530°C) is slightly higher than that of S6 (450°C), while its surface hardness is much higher than the later. As our coating was a
mixed film containing LiTaO₃ and tantalum oxides, we could not attribute it to the contribution of pure product with regard to hardness. In fact, it was their combined effect affecting the change of surface hardness.

Table 2. Film thickness of LiTaO₃ coated samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
<th>S7</th>
</tr>
</thead>
<tbody>
<tr>
<td>d/μm</td>
<td>1.5</td>
<td>3.0</td>
<td>4.1</td>
<td>1.7</td>
<td>3.7</td>
<td>2.3</td>
<td>3.3</td>
</tr>
</tbody>
</table>

3.4. Immersion Corrosion Tests

Ta substrate and samples coated by LiTaO₃ thin film were immersed into 10 wt% NaOH solution for 96h to study their anti-corrosion performance. Mass change of each specimen was registered with results exhibited in Fig. (8a) while corresponded corrosion rate being calculated according to Eqn. (1) and displayed in Fig. (8b). Note, all samples coated by LiTaO₃ thin film showed lower mass loss (< 4 mg), comparing to that of Ta substrate (up to 23 mg). This is a clear indication such that Ta substrate becomes almost 6x more resistive to corrosion upon anodic oxidation. Corrosion rate of $8 \times 10^{-6}$ g.cm⁻².h⁻¹ was obtained for coated samples instead of $47 \times 10^{-6}$ g.cm⁻².h⁻¹ for Ta substrate. Corresponding corrosion inhibition efficiency was calculated according to Eqn. 2 and listed in Table 3. It is clear that all coated samples showed high corrosion inhibition efficiency of over 83%, suggesting that formed LiTaO₃ thin film as well as tantalum oxides inhibit the corrosion of NaOH alkali solution. Samples of S2, S3 and S7 had the minimum corrosion rate (Fig. 8b) and maximum corrosion inhibition efficiency (Table 3) with high resistance for corrosion. Accounting for energy saving and production efficiency in practical application, however, lowering temperature or shortening reaction time will reduce power consumption and cost. Thus, S2 (synthesis condition is 490°C-5V-3h) was regarded as optimal among all samples.

Fig. (7). Hardness of coated samples synthesized as function of (a) time, (b) voltage and (c) temperature.

Fig. (8). Mass change (a) and corrosion rate (b) of samples after immersion test.
SEM images of pure Ta and sample coated by LiTaO\textsubscript{3} thin film (S2) are depicted in Fig. (9) (Fig. 9a from pure Ta, Figs. 9b and 9c from S2). We can see clearly that pure Ta was indeed eroded by NaOH solution in almost all range leading to the uneven surface with many holes (Fig. 9a), corresponding to the maximum mass loss showed in Fig. (8a). Sample S2, however, was corroded slightly with only a few small pits (Fig. 9b) and appeared on a nearly smooth surface. One magnified image (see Fig. 9c, the insert of Fig. 9b) may demonstrate a pit eroded slightly by NaOH solution. These contrastive experiments showed that LiTaO\textsubscript{3} thin film can prevent Ta substrate from ionic attack in NaOH solution. We can also relate those results to mass loss of Fig. (8a) to demonstrate the effect of LiTaO\textsubscript{3} thin film on anticorrosion.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S0</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
<th>S7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta m$/g</td>
<td>0.023</td>
<td>0.004</td>
<td>0.001</td>
<td>0.001</td>
<td>0.003</td>
<td>0.002</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>$IE_{corr}$</td>
<td>-</td>
<td>0.83</td>
<td>0.96</td>
<td>0.96</td>
<td>0.87</td>
<td>0.91</td>
<td>0.91</td>
<td>0.96</td>
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</tbody>
</table>

Fig. (9). Surface morphologies of samples after immersion test: (a) pure Ta, (b) and (c) LiTaO\textsubscript{3} coated.

Fig. (10). OCPs (a) and potentiodynamic polarization curves (b) of samples immersed in 10 wt% NaOH solution at 50°C as function of time.

SEM images of pure Ta and sample coated by LiTaO\textsubscript{3} thin film (S2) are depicted in Fig. (9) (Fig. 9a from pure Ta, Figs. 9b and 9c from S2). We can see clearly that pure Ta was indeed eroded by NaOH solution in almost all range leading to the uneven surface with many holes (Fig. 9a), corresponding to the maximum mass loss showed in Fig. (8a). Sample S2, however, was corroded slightly with only a few small pits (Fig. 9b) and appeared on a nearly smooth surface. One magnified image (see Fig. 9c, the insert of Fig. 9b) may demonstrate a pit eroded slightly by NaOH solution. These contrastive experiments showed that LiTaO\textsubscript{3} thin film can prevent Ta substrate from ionic attack in NaOH solution. We can also relate those results to mass loss of Fig. (8a) to demonstrate the effect of LiTaO\textsubscript{3} thin film on anticorrosion.

### 3.5. Electrochemical Measurements

OCP and potentiodynamic polarization curves of Ta substrate and LiTaO\textsubscript{3} thin film coated sample are presented in Fig. (10). Compared to continuously OCP drop of pure Ta (started at -0.754V), that of coated sample remains almost stable (remained at -0.096V) (Fig. 10a). This drop of OCP of pure Ta with time is indicative of dissolution of protective oxide film formed naturally in air. Similar behavior has been reported for Niobium (Nb) in NaOH solution [33]. In addition, the OCP
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value of LiTaO₃ coated sample is higher than that of Ta substrate with less chance to be eroded in NaOH solution.

Besides the difference in OCPs, shape of their potentiodynamic polarization curves are alike (Fig. 10b), indicated that possible erosion reactions occurred at metal-solution interface should be similar. Of Tafel behavior, corrosion current density of these samples was obtained by extrapolation of linear fitting. Tafel values of Ta substrate and LiTaO₃ coated sample are listed in Table 4, calculation of corrosion current density of pure Ta and LiTaO₃ coated sample to be 6.4×10⁻⁷ and 4.7×10⁻⁹ A.cm⁻². Note here, of higher corrosion potential and about two orders lower corrosion current density, corrosion reactions between LiTaO₃ thin film and NaOH must be very weak. Fig. (11) shows surface morphologies of samples after potentiodynamic polarization test (Fig. 11, a for pure Ta and b for LiTaO₃ coated sample). As can be seen from Fig. (11a), there are many stripes and a few holes appeared in the surface of Ta substrate. It is likely that electrochemical corrosion occurred on the surface during the polarization test. However, the surface morphology of LiTaO₃ coated sample (Fig. 11b) does not change after polarization test. These results showed that the corrosion resistance has been improved after coating (by LiTaO₃).

Table 4. Corrosion potential and corrosion current density of tested samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_{corr}$ (mV/SCE)</th>
<th>$I_{corr}$ (A/cm²)</th>
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<tbody>
<tr>
<td>S0: Pure Ta</td>
<td>-754</td>
<td>6.4×10⁻⁷</td>
</tr>
<tr>
<td>S2: with LiTaO₃ coating</td>
<td>-96</td>
<td>4.7×10⁻⁹</td>
</tr>
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</table>

Nyquist and Bode plots of tested samples are depicted in Figs. (12) and (13). Nyquist plot of Ta displays one semicircle (Fig. 12a) while Bode plot of Ta shows a linear relationship between and with slope of -0.97 and phase angle of -87° for high frequency range (Fig. 13a). These are characteristics of predominantly capacitive behavior. In contrast, Nyquist plot of LiTaO₃ coated sample shows two capacitance circles (Fig. 12b) with impedance higher than that of Ta. Bode plot of Fig. (13b) depicts two linear relationships between and with one slope of -0.63 in low frequency range, another -0.59 in high frequency range, accompanying with phase angle of -48°.

![Fig. 11. Surface morphologies of samples after potentiodynamic polarization test: (a) pure Ta and (b) LiTaO₃ coated.](image)

![Fig. 12. Nyquist plots of tested samples in 10 wt% NaOH solution at 50°C: (a) pure Ta, (b) LiTaO₃ coated.](image)

To illustrate the details of Nyquist plots, a commonly accepted equivalent circuit is employed by considering the properties of corrosive solution and samples, as shown in Fig. (14). Where $R_0$ is the resistance of electrolyte, $R_1$ is the...
resistance of charge transfer, $R_2$ is the resistance of LiTaO$_3$ coating, $C$ is the capacitor resistance, CPE 1 and CPE 2 are the constant phase elements related to capacitance of double layer and LiTaO$_3$ film, respectively. The impedance of CPE is defined as

$$Z_{\text{CPE}} = \frac{1}{Y(j\omega)^n} \quad (10)$$

Values of fitted equivalent circuit parameters are listed in Table 5. Note here, LiTaO$_3$ coated sample showed larger values of capacitor resistance (for CPE 1 and CPE 2) and charge transfer resistance ($R_1$) than those of pure Ta substrate. The former had a very high resistance of passive film with value of $7.949 \times 10^5$ $\Omega$·cm$^2$ ($R_2$). Notice that the resistance of $R_2$ referred to the total value of passive film, as our coating being mixed film containing LiTaO$_3$ and tantalum oxides. Therefore, we could not attribute it to the contribution of pure product with regard to corrosion resistance. Generally speaking, the larger value of the impedance, the better corrosion resistance of the sample. According to these analysis, anticorrosion performance of LiTaO$_3$ coated sample must be superior to that of pure Ta substrate. This is in accordance with our findings of immersion tests. The protective LiTaO$_3$ thin film coated on Ta surface can effectively block reactants of NaOH solution from attacking the surface underneath.

**CONCLUSION**

1) LiTaO$_3$ thin film has been prepared and coated on Ta substrate by anodic oxidation in molten LiNO$_3$. Both content and hardness of LiTaO$_3$ coating increase gradually with synthesized time, voltage and temperature.

2) Morphology of LiTaO$_3$ coating changed with synthesized voltage and temperature.

3) Coated samples have smaller mass loss ($<4$ mg) and corrosion rate ($8 \times 10^{-6}$ g·cm$^{-2}$·h$^{-1}$) in immersion corrosion tests compared to those of pure Ta substrate (23 mg and $47 \times 10^{-6}$ g·cm$^{-2}$·h$^{-1}$).

4) Coated samples have demonstrated lower corrosion current density ($4.7 \times 10^{-9}$ A·cm$^{-2}$), higher impedance ($7.949 \times 10^5$ $\Omega$·cm$^2$) and 6-times better corrosion resistance in NaOH solution.
AUTHOR CONTRIBUTIONS

In this research work, Likun Hu designed and conducted the experiments and experimental testing; Dengfeng Xu, Zhi Peng and Axi Xie provided the reagents/materials/equipment for the experiments; Sicheng Yuan and Panping Xie gave some help for data analysis; Likun Hu wrote the manuscript and Feng Zheng revised the paper for submission.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The data supporting the findings of the article is available in the web of "figshare", the detailed link is [https://figshare.com/s/cb9dadc0bab367d9152e].

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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