

Short Communication

Effect of Hydration on Porous Anodic Alumina with Large Interpore Distances during Anodization with Ultrahigh Voltage

Jie Wang¹, Lin Jiang¹, Ning Peng^{1,2,*}, Qili Tan¹, Libo Liang²

¹ Guangxi Key Laboratory of Electrochemical and Magnetochemical Functional Materials, Guilin University of Technology, 541004, Guilin, China

² Institute of Technology Research and Development of Electronic Aluminum Foil, Guangxi Hezhou Guidong Electronics Technology Co. Ltd., 542800 Guangxi, China

*E-mail: ncdxclpn@163.com (N. Peng).

Received: 2 November 2020 / Accepted: 17 December 2020 / Published: 31 January 2021

The effects of the hydrated alumina film obtained from hydration process on the porous anodic alumina (PAA) film fabricated under the ultrahigh voltage in a mixed electrolyte were investigated. It is found that the hydrated alumina film can enhance the voltage of anodization and facilitate the uniform growth of the PAA film. The suitable thickness of the hydrated alumina film can be used to facilitate the self-assembly formation of the unite cell on porous PAA film. Besides, it is found that some of aluminum nanocones is presented on the sidewalls of the nanodents, due to the relatively poor self-assembly of the nano-structural units, which result in the inadequacy transformation of the aluminum between the nano-structural units to the alumina. These finding may can be used for fabricating the aluminum nanostructure on the aluminum surface directly.

Keywords: Porous film; Hydration; ultrahigh voltage; nanocones; Phosphoric acid;

1. INTRODUCTION

Porous anodic alumina (PAA) film obtained by anodization under various voltage have been extensively used in decoration of metal/alloy coating to resist corrosion attack [1]. Along with the advancement of science and technology, the PAA structure is gradually served as the advanced functional materials in various field, including energy storage, templates of nanofabrications, carrier of catalyst, and so on [2, 3]. The self-assembly PAA film with nanoscale honeycomb structure is characterised by excellent chemical stability, easily fabrication and tunable pore features [4, 5]. In terms of tunable pore structures, the fabrication of the PAA film with the larger interpore distances (D_{int}) is still extensively investigated by the researchers, which is derived from the limited applications of the nano-porous structures of PAA film [6-8].

It is well recognized that the value of D_{int} will be in proportion to the applied anodization voltage [9-12]. As to a certain electrolyte system, the higher anodization voltage, the larger the D_{int} . Thus, the direction of the investigation is how to enhance the anodization voltage and concomitantly restrain the undesired burning or alumina breakdown. On the one hand, some of organic carboxylic acids with strong polarity and low dissociation constants, including ethylene glycol, tartaric acid, malonic acid, and so on, can be used to improve the undesired burning of alumina, resulting in the anodization voltage enhanced appropriately [2, 7, 13-15]. To the best of our knowledge, however, the voltage window is still narrow when the novel reagent is used as the anodized electrolyte. To increase the voltage window of anodization, a mixed electrolyte with various acids is proposed and used. For example, Chen used a mixed solution, including citric acid, phosphoric acid and ethylene glycol, to perform anodization at ultra-high voltage [16]. The corresponding value of D_{int} is achieved in the range of 1400~2036 nm, whereas the uniform distribution of the self-assembly unit cell obtained on the PAA film is unsatisfied. On the other hand, a thin pre-existed film forming on the Al substrate by using hard anodization can be used for resisting the local burning or catastrophe, so that the voltage window is increased obviously [17, 18]. However, to our knowledge, the fabricating process of the pre-existed film and the subsequent obtention of PAA film is usually performed in the same electrolyte. In our previous work, a hydrated alumina film obtained by hydration treatment is successfully fabricated on Al substrate to enhance the self-assembly structure of PAA film under an excess anodization voltage of 60 V in 0.3 M oxalic acid [19]. It is indicated that the hydrated alumina film can be served as the role of a thin pre-existed film. Actually, the hydrated alumina film fabricated on Al substrate will consist of a porous alumina layer and a dense alumina barrier layer, where the former can suitably improve the self-ordered array of PAA film and the latter can enhance the withstand voltage of Al substrate. Whereas, under the ultra-high voltage of aluminum anodization, the effects of the hydrated alumina film on the formation of PAA film with large interpore distances is unexplored. For evaluation the role of hydration in improving the interpore distances of PAA film under the ultra-high voltage. In this work, the hydrated alumina films with different thickness were firstly obtained by hydration process of Al sheet, and then the as-prepared aluminum sheets were carried out anodization under an ultra-high voltage in a mixed solution consisting of citric acid, ethylene glycol and phosphoric acid. The self-ordered array and the interpore distances of the obtained PAA film were investigated carefully. The investigation of the present work is to explore insight regarding the influence of hydration on ultra-large interpore distances of anodic alumina film obtained by anodization of ultra-high voltage.

2. EXPERIMENTAL

Aluminum sheets (high purity 99.999%, 1.25 mm thick, JOINWORLD, China) with the sizes of 20 mm × 20 mm were firstly ultrasonic cleaned in acetone and ethanol for 10 min to remove contaminants. After that, the clear samples were electropolished at 0 °C in a V/V =1:4 mixture of perchloric acid and ethanol under voltage of 20 V for 2 min to obtain a mirror surface. Then the as-prepared Al sheets were performed hydration in deionized water at 97±2 °C for various times. The Al sheets with different thickness of hydrated alumina film were carried out mild anodization (MA process)

at ultrahigh voltage of 700 V and 800 V at 0 ± 1 °C for 5 h in a mixed electrolyte containing 250 ml PEG-400, 250 ml 2wt.% citric acid and 1 ml 0.1 wt.% phosphoric acid [16]. After the anodization, the samples were similar electropolished at 0 °C in the above solution under voltage of 15 V for 10 s to observe the porous anodic alumina clearly. In order to expose the aluminum substrate, some of the as-prepared specimens were immersed into a mixed solution of 1.8 wt.% CrO_3 and 6 wt.% H_3PO_4 for 12 h at 60 °C. Besides, the pore enlargement was performed by dipping the as-anodized Al sheets into a 5 wt.% phosphoric acid at 30 °C for 1 h. The obtained morphology, including the hydrated alumina film, the anodic alumina film and the exposed aluminum substrate, were carefully observed by Field Emission Scanning Electron Microscope (FESEM, JSM-6610A, Japan).

3. RESULTS AND DISCUSSION

Fig. 1 shows the SEM images of the hydrated alumina film fabricated by the hydration on the electropolished aluminum foils at 90 ± 2 °C for the duration of 1 min and 15 min. After the hydration process, it can be seen that the aluminum surface was entirely covered by the hydrated alumina film. And the morphology of the alumina film varies with the hydration time. It is well known that the hydrated alumina film obtained by the hydration are composed of a porous alumina layer and a dense alumina barrier layer. The dense barrier layer was generated at the interface of aluminum substrate/porous layer[20, 21]. As to the porous layer of the hydrated alumina film, the thin ‘cornflake’ structure obtained under hydration of 1 min, as shown in Fig. 1a, is thickened progressively and gather together finally, as shown in Fig. 1b. As to the barrier layer of the hydrated alumina film, it was indicated in our previous work that the dense alumina barrier layer can facilitate the enhancement of the anodizing voltage[19, 22]. It can be expected that the increasing thickness and compactness may be improve the anodizing voltage further.

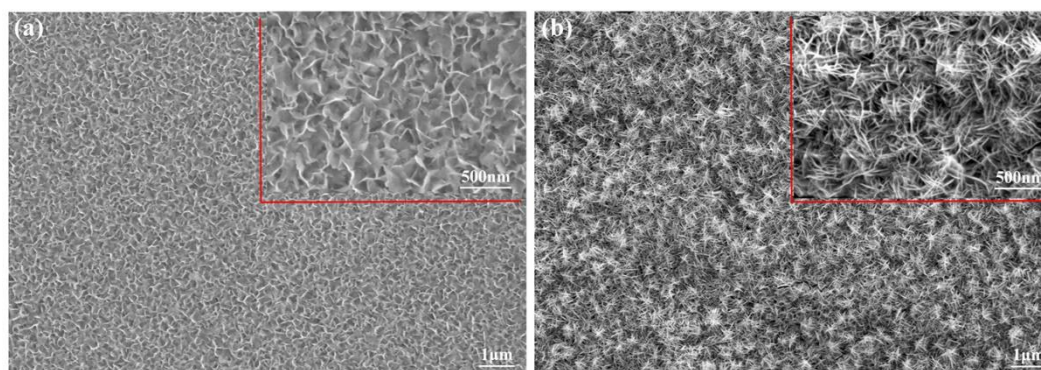


Figure 1. SEM images of the hydrated alumina film obtained from the hydration treatment of aluminum foils at 90 ± 2 °C for (a) 1 min, (b) 15 min.

The SEM surface images of the PAA film fabricated by the anodization of the electropolished aluminum foils at potential of 700 V in a mixed electrolyte containing 250 ml PEG-400, 250 ml 2wt.%

citric acid and 1 ml 0.1 wt.% phosphoric acid are shown in Fig. 2. It can be seen from Fig. 2a that under the ultrahigh voltage of anodization, the electropolished aluminum foil without hydration process hardly generate the uniform PAA film, where only a few nanoporous cells were formed randomly. Especially, the undesired local burning of alumina, as marked with the blue arrow in Fig. 2a, were also generate under the ultrahigh voltage, which indicate that the bare aluminum foil cannot perform the rigorous anodization in the above electrolyte [23, 24]. In contrast, after the ultrahigh voltage of anodization, the samples with hydrated alumina film produce the PAA film which is uniformly distributed on the aluminum surface. And the nanoporous structures, as shown in Fig. 2b and c, are also evenly distributed on the aluminum surface. As can be expected, the hydrated alumina film, served as the role of the pre-anodic oxide film formed in the HA anodization process, can increase the voltage of anodization. However, it is found that the surface morphology of the PAA film in Fig. 2b is relatively rough by comparison with the surface morphology in Fig. 2c, implying that the various morphologies of the hydrated alumina film are the major factors responsible for the morphologies difference in Fig. 2b and c. After statistics the interpore distance of the nanoporous on the PAA film, the average value of the interpore distance is $1.55\ \mu\text{m}$ in Fig. 2b and $1.62\ \mu\text{m}$ in Fig. 2c.

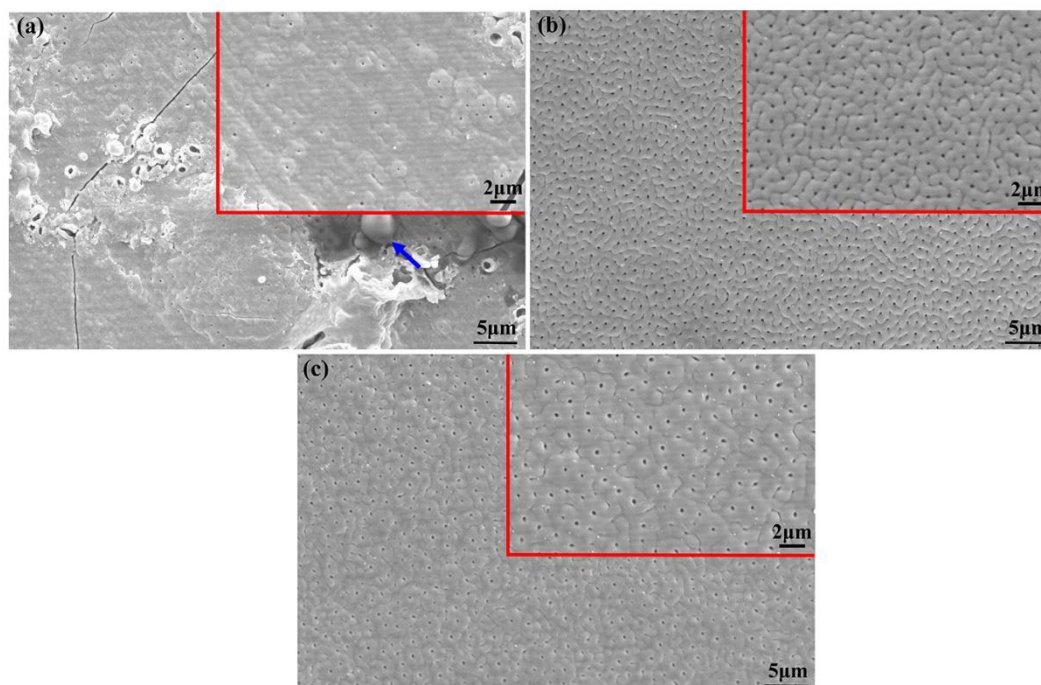


Figure 2. SEM images of PAA film fabricated by anodization of the electropolished aluminum foil (a) without hydration process and with (b) 1min and (c) 15 min hydration process. The applied potential is 700 V in a mixed electrolyte containing 250 ml PEG-400, 250 ml 2wt.% citric acid and 1 ml 0.1 wt.% phosphoric acid.

And the average sizes of the nanopore is 235 nm in Fig. 2b and 256 nm in Fig. 2c. It can be seen from Fig. 2 that the hydrated alumina film obtained by hydration treatment was found to strongly affects

not only the endurance of the anodization voltage, but as well the surface appearance and its nanoporous structure, including the size and interpore distance. In our previous work, the anodization process was performed in a solution of 60 V in 0.3 mol/L oxalic acid electrolyte. And it has been proved that the barrier layer included in hydrated alumina film can increase the voltage of anodization, and the porous layer can observably improve the self-ordered array of nanostructure [19, 25]. It is indicated in the present work that under the ultrahigh voltage of anodization, the hydrated alumina film obtained by hydration process also can be to play a role of pre-existed film in PAA film fabrication.

Fig. 3 shows the nanoporous structure obtained by dipping the corresponding PAA film of Fig. 2b and c in a 5 wt.% phosphoric acid at 30 °C for 1 h. It can be seen from the Figure that the enlarged nanoporous are uniformly distributed on the entire PAA film. However, the integrity of the PAA film in Fig. 3 is distinguishing. The integrity of the PAA film in Fig. 3a is superior to that in Fig. 3b. In Fig. 3b, the convex cell and concave defects, marked with blue and yellow arrows respectively, were observed clearly. This imperfection of the PAA film in Fig. 3b can be attributed to the fact that the gather together of the 'cornflake' structure of the porous layer, as shown in Fig. 1b, could weaken its effect to tunable self-ordered array of PAA film [26, 27]. Therefore, the thickness of the hydrated alumina film obtained by hydration process should be suitable to ensure the integrity of the PAA film.

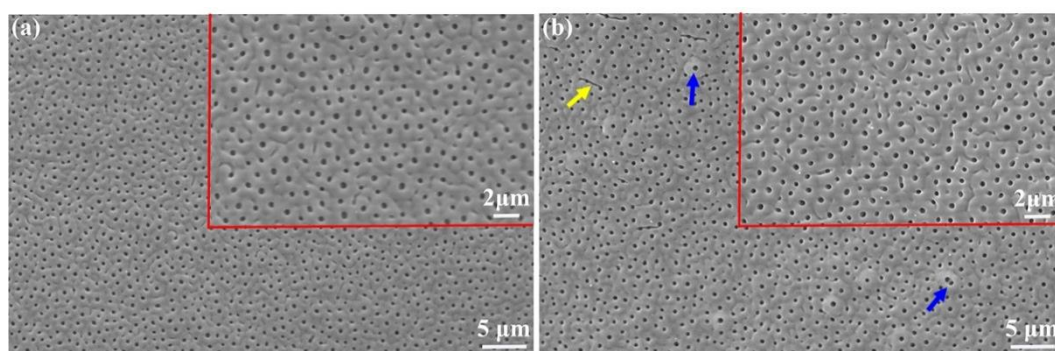


Figure 3. The SEM images of the nanoporous structure obtained by dipping the corresponding PAA film of Fig. 2b and c in a 5 wt.% phosphoric acid at 30 °C for 1 h.

After the first step anodization under the ultrahigh voltage and the obtained PAA films were stripped clearly, the nanodents on the aluminum substrate is presented in Fig. 4. Due to the first anodization and the ultrahigh voltage of anodization, the arrangement of the nanodents is disordered and the corresponding size is uneven. However, it is surprising that some of aluminum nanocones is presented on the sidewalls of the nanodents, as marked with the blue arrow in Fig. 4. The generated nanocones underneath the PAA film can be attributed to the poor self-assembly of the nano-structural units, resulting in the inadequacy transformation of the aluminum between the nano-structural units to the alumina. These notably finding may be used for fabricating the aluminum nanostructure on the aluminum surface directly.

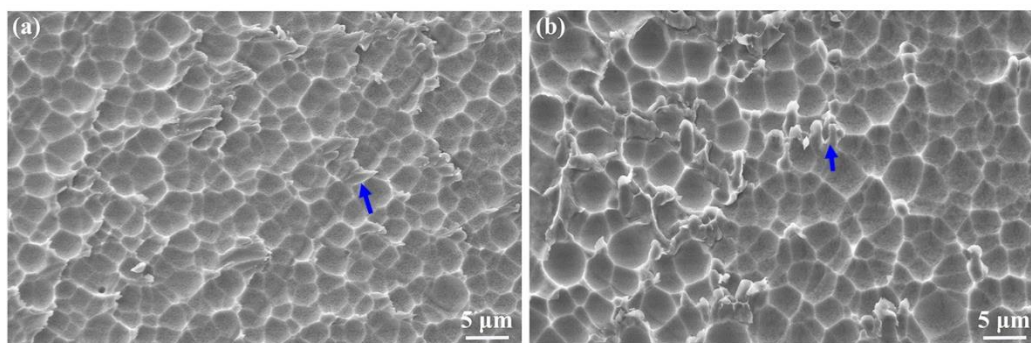


Figure 4. The SEM images of the nanodents on the aluminum substrate after stripping the corresponding PAA film that is depicted in Fig.3.

To investigate the higher voltage of anodization, the electropolished aluminum foil with 15 min hydration treatment were performed anodization under the voltage of 800 V in a mixed electrolyte containing 250 ml PEG-400, 250 ml 2wt.% citric acid and 1 ml 0.1 wt.% phosphoric acid. It can be seen from Fig. 5a that under the ultrahigh voltage, the obtained PAA film cannot uniformly cover on the aluminum surface. Due to the large strain, the crack is produced on the PAA film. The magnified morphology of the PAA film is showed in Fig. 5b, where the nano-structural unit is also formed during the anodization. Meanwhile, it can be seen that the nanopore was found to not only generated on the center of the unit, but as well at every angle of the hexagon, as shown the mark in Fig. 5b. The mechanism of the nanopore distribution on the aluminum foil with hydrated alumina film under the ultrahigh voltage of anodization can be investigated further. Therefore, it is indicated that the withstand voltage of anodization improved by the hydrated alumina film is limited.

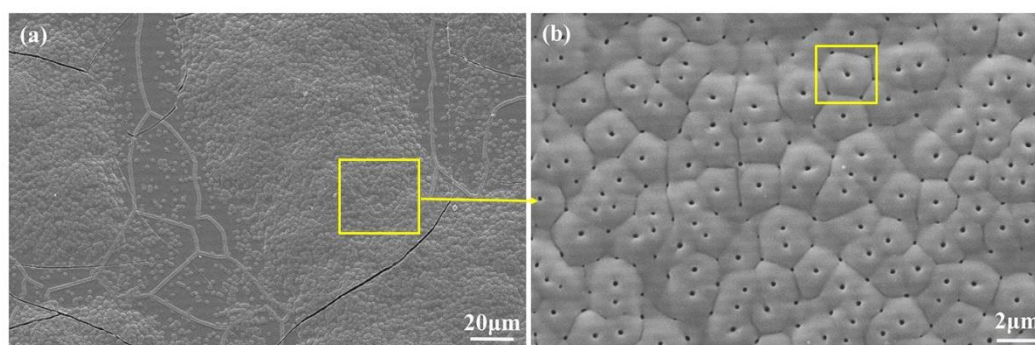


Figure 5. The SEM images of PAA film fabricated by anodization of the electropolished aluminum foil with 15 min hydration process. The applied potential is 800 V in a mixed electrolyte containing 250 ml PEG-400, 250 ml 2wt.% citric acid and 1 ml 0.1 wt.% phosphoric acid.

4. CONCLUSION

In this work, based on the previous investigation, the effects of the hydrated alumina film obtained by hydration process on the PAA film with large interpore distances were investigated

detailedly. It is demonstrated that under the 700 V voltage of anodization, the obtained hydrated alumina film on the aluminum surface can facilitate the uniform growth of the PAA film, where the nanopore with various sizes was generated. However, when the duration of hydration process was prolonged, the progressively thickened and assembled hydrated alumina film has a negative self-assembly impact, resulting in the uniformity of the PAA film decreased. Besides, it is amazingly found that some of nanocones of aluminum is presented on the sidewalls of the nanodents, which can be used for fabricating the aluminum nanostructure on the aluminum surface directly. When the voltage of anodization is up to 800 V, the hydrated alumina film cannot served as the role of the pre-existed film to withstand the voltage, which result in the PAA film is generated on aluminum surface randomly.

ACKNOWLEDGMENTS

This research was supported by the Young People Fund of the Guangxi Science and Technology Department (No. 2018GXNSFBA050007), the Doctor's Scientific Research Foundation of Guilin University of Technology (No. GUTQDJJ2018050), The provincial university student innovation and entrepreneurship training programs (No. 202010596165), Science & Technology Base and Special Talent (GUIKE-AD19110066) and the Innovation-Driven Development Project of Hezhou City (ZX1907001).

COMPLIANCE WITH ETHICAL STANDARDS

CONFLICT OF INTEREST

We have not any financial/commercial conflicts of interest.

DATA AVAILABILITY

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations. They will be shared upon reasonable request.

References

1. H. Masuda, and K. Fukuda, *Sci.*, 268 (1995) 4.
2. T. Kikuchi, D. Nakajima, J. Kawashima, S. Natsui, and R.O. Suzuki, *Appl. Surf. Sci.*, 313 (2014) 10.
3. P. Chowdhury, A.N. Thomas, M. Sharma, and H.C. Barshilia, *Electrochim. Acta*, 115 (2014) 657.
4. L. Zaraska, W.J. Stepniowski, E. Ciepela, and G.D. Sulka, *Thin Solid Films*, 534 (2013) 155.
5. Y. Li, N. Peng, W. Shang, Y. Wen, and Y. He, *J. Electrochem. Soc.*, 167 (2020) 1508.
6. W.J. Stepniowski, A. Nowak-Stepniowska, and Z. Bojar, *Mater. Charact.*, 78 (2013) 79.
7. Y. Ma, Y. Wen, J. Li, J. Lu, Y. Li, Y. Yang, C. Feng, C. Hao, Z. Zhang, J. Hu, and R. Sun, *J. Electrochem. Soc.*, 165 (2018) 311.
8. H. Zhao, L. Liu, and Y. Lei, *Front. Chem. Sci. Eng.*, 12 (2018) 481.
9. D.I. Petukhov, K.S. Napolskii, M.V. Berekchiyan, A.G. Lebedev, and A.A. Eliseev, *ACS Appl. Mater. Interfaces*, 5 (2013) 7819.
10. K. Chernyakova, A. Ispas, R. Karpicz, G. Ecke, I. Vrublevsky, and A. Bund, *Surf. Coat. Technol.*, 394 (2020) 125.
11. M. González-Castaño, C. Cancellieri, X. Maeder, E. Hack, and P. Schmutz, *Appl. Surf. Sci.*, 505 (2020) 144.

12. S. Pan, L. Liang, B. Lu, and H. Li, *J. Alloys Compd.*, 823 (2020) 153.
13. W. Lee, and S.J. Park, *Chem. Rev.*, 114 (2014) 7487.
14. T. Kikuchi, A. Takenaga, S. Natsui, and R.O. Suzuki, *Surf. Coat. Technol.*, 326 (2017) 7.
15. A. Brzózka, A. Brudzisz, D. Rajska, J. Bogusz, R. Palowska, D. Wójcikiewicz, and G.D. Sulka, *Surf. Coat. Technol.*, 456(2020) 35.
16. X. Chen, D. Yu, L. Cao, X. Zhu, Y. Song, H. Huang, L. Lu, and X. Chen, *Mater. Res. Bull.*, 57 (2014) 116.
17. S. Tang, H. Zhou, S. Liu, C. Fu, Z. Huang, P. Huang, and Y. Kuang, *Mater. Chem. Phys.*, 139 (2013) 339.
18. M.R. Song, L. Song, S.L. Xu, Z.J. Zhang, *Electrochim. Acta*, 53 (2008) 7198.
19. Y. Li, N. Peng, Y. Wen, and L. Liang, *Microporous Mesoporous Mater.*, 306 (2020) 110.
20. P.R. Underhill, and A.N. Rider, *Surf. Coat. Technol.*, 192 (2005) 199.
21. Y. Chang, Z. Ling, Y. Li, and X. Hu, *Electrochim. Acta*, 93 (2013) 241.
22. A.C. Geiculescu, and T.F. Strange, *Thin Solid Films*, 445 (2003) 105.
23. K.Q. Zhang, and S.S. Park, *Surf. Coat. Technol.*, 342 (2018) 159.
24. K.Q. Zhang, and S.S. Park, *Appl. Surf. Sci.*, 477 (2019) 44.
25. C.K. Chung, W.T. Chang, M.W. Liao, H.C. Chang, and C.T. Lee, *Electrochim. Acta*, 56 (2011) 6489.
26. J. Liu, S. Liu, H.H. Zhou, Z.Y. Huang, C.P. Fu, and Y.F. Kuang, *Thin Solid Films*, 552 (2014) 75.
27. H. Asoh, K. Nishio, M. Nakao, T. Tamamura, and H. Masuda, *J. Electrochem. Soc.*, 148 (2001) 152

© 2021 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).