



Electrochemical polymerization of dopamine with/without subsequent PLLA coating on Mg-Zn-Y-Nd alloy

Ci Song^a, Yongxin Yang^a, Yifan Zhou^{a,b}, Liguang Wang^{a,b,c,*}, Shijie Zhu^{a,b,c}, Jianfeng Wang^{a,b}, Rongchang Zeng^d, Yufeng Zheng^e, Shaokang Guan^{a,b,c,*}

^a School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

^b Henan Key Laboratory of Advanced Magnesium Alloys, Zhengzhou 450002, China

^c Key Laboratory of Advanced Materials Processing & Mold Ministry of Education, Zhengzhou 450002, China

^d College of Material Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China

^e State Key Laboratory for Turbulence and Complex System and Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

ARTICLE INFO

Article history:

Received 5 March 2019

Received in revised form 25 April 2019

Accepted 29 April 2019

Available online 29 April 2019

Keywords:

Electrodeposition

Surface

Mg-Zn-Y-Nd alloy

Polydopamine

Galvanostat

Sodium salicylate

ABSTRACT

The high surface roughness of dip polydopamine (dPDA) coating on magnesium alloy could decrease the quality of secondary modification. In the present study, we report an electropolymerized dopamine (ePDA) coating on Mg-Zn-Y-Nd alloy from sodium salicylate aqueous solutions by galvanostat method to address this problem. The coating formation process and coating structure were investigated. Then, a Poly (L-lactic acid) (PLLA) coating was prepared on ePDA and dPDA treated samples. The SEM results reveal that the ePDA film appeared to be more uniform than dPDA coating and was doped with salicylate and magnesium ions. ASTM D3359-09 “Tape test” shows excellent adhesion of the ePDA/PLLA layer. The electrochemical impedance spectroscopy and polarization curves demonstrate ePDA/PLLA film has a better corrosion resistance than dPDA/PLLA film, owing to the structural difference of polydopamine anchoring layer.

© 2019 Published by Elsevier B.V.

1. Introduction

The poor corrosion resistance of Mg alloys is a vital challenge to achieve wide application in bioimplants [1]. Polydopamine (PDA) has excellent adhesion properties and could improve the corrosion resistance of Mg alloys as an intermediate coating [2–5]. In the preparation of dip polydopamine (dPDA) coating, $\text{Mg}(\text{OH})_2$, H_2 and numerous PDA aggregates could be formed [6,7]. These lead to high roughness of the dPDA coating, and thereby reduce the quality of the subsequent modification. A smooth electropolymerized dopamine (ePDA) coating is more favorable for the secondary modification compared with dPDA coating [6,8]. To our knowledge, there is still no report related to ePDA film on Mg alloy surfaces possibly on account of anodic dissolution of Mg alloys during the electrodeposition process. Recently, taking the advantages of sodium salicylate (SS), Turhan *et al.* [9] prepared polypyrrole coatings on AZ91D alloy and the anodic dissolution of Mg alloy was significantly inhibited.

In this study, we prepared the ePDA films on Mg-Zn-Y-Nd alloy by galvanostat method in SS aqueous solution. The surface morphology and chemical constitution of ePDA films were characterized. Furthermore, as a proof-of-concept, Poly (L-lactic acid) (PLLA) was prepared on the surface of ePDA, dPDA and Mg alloy samples to investigate the effect of PDA coatings on composite coatings.

2. Experimental details

The detailed information of chemicals and materials are consulted in [Supporting information 2](#). 1 M SS solution was prepared by distilled water and bubbled with high purified nitrogen for 20 min to remove oxygen, then DA was dissolved into the solution at a concentration of 2 g/L. The pH of the solution decreases to about 6.8 and was not readjusted. The electropolymerization of DA was carried out by galvanostat method with a standard three-electrode cell by RST 5200F electrochemical workstation (Shiruisi, Zhengzhou, China), where saturated calomel electrode (SCE) and platinum electrode acted as the reference electrode and counter electrode, respectively. The current density was 14.5 mA/cm^2 and lasted for 40 s. The solution temperature was

* Corresponding authors at: School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China.

E-mail addresses: lgwang@zzu.edu.cn (L. Wang), skguan@zzu.edu.cn (S. Guan).

kept at 25 °C. Afterwards, each sample was rinsed three times with ethanol and dried at 80 °C for 1 h.

The dPDA, PLLA and PDA/PLLA coating were fabricated by dipping method. All these experimental steps are consulted in [Supporting information 3](#). And the subsequent characterization experiments are consulted in [Supporting information 4](#).

3. Results and discussion

The N1s high-resolution patterns of the ePDA, and ePDA* (Ar-ions etching 120 s) samples are shown in the Fig. 1a and b, respectively. There is almost no signal in the N1s pattern of ePDA. However, a peak at 398.8 eV for -NH- species appears in the N1s spectrum of ePDA*, confirming the anchoring of ePDA film.

The O1s spectra of ePDA (Fig. 1c) presents two fitted peaks, one at 531.5 eV is assigned to the C=O and second (532.2 eV) is linked to the O=C-O⁻ in salicylate anions. It could be inferred that the absence of N1s signal of ePDA is mainly caused by salicylic acid

precipitated on the ePDA film. During polymerization process, H⁺ produced by oxidation of DA could lead to the protonation of salicylate anion [10], and then salicylic acid crystallizes due to its low solubility in water [11]. As for O1s signal of ePDA*, apart from the C=O species at 530.8 eV and the C-O species at 531.6 eV, a newly peak at 529.0 eV is responsible for Mg-O species, suggesting that Mg²⁺, produced by anodic dissolution, participated in the formation of the coating. The XPS data of Mg and dPDA were consulted in [Supporting Information 5](#).

The ATR-FTIR of ePDA and dPDA samples are presented in Fig. 1e. The peaks appeared at 1560 cm⁻¹ and 1430 cm⁻¹ are attributed to the C=C stretching vibration [7]. The peak around 1270 cm⁻¹ may be due to the stretching vibration of C-O species and the appearance of bands at 1364 cm⁻¹ in ePDA sample is possibly a cue to the appearance of CNC stretching vibration [6]. These results suggest that the ePDA film was successfully deposited. Additionally, the peak appears at 1640 cm⁻¹ could be assigned to the skeleton vibration of the benzene ring in the salicylate ions. It is worth mentioning that a C=N peak at 1491 cm⁻¹ in dPDA is

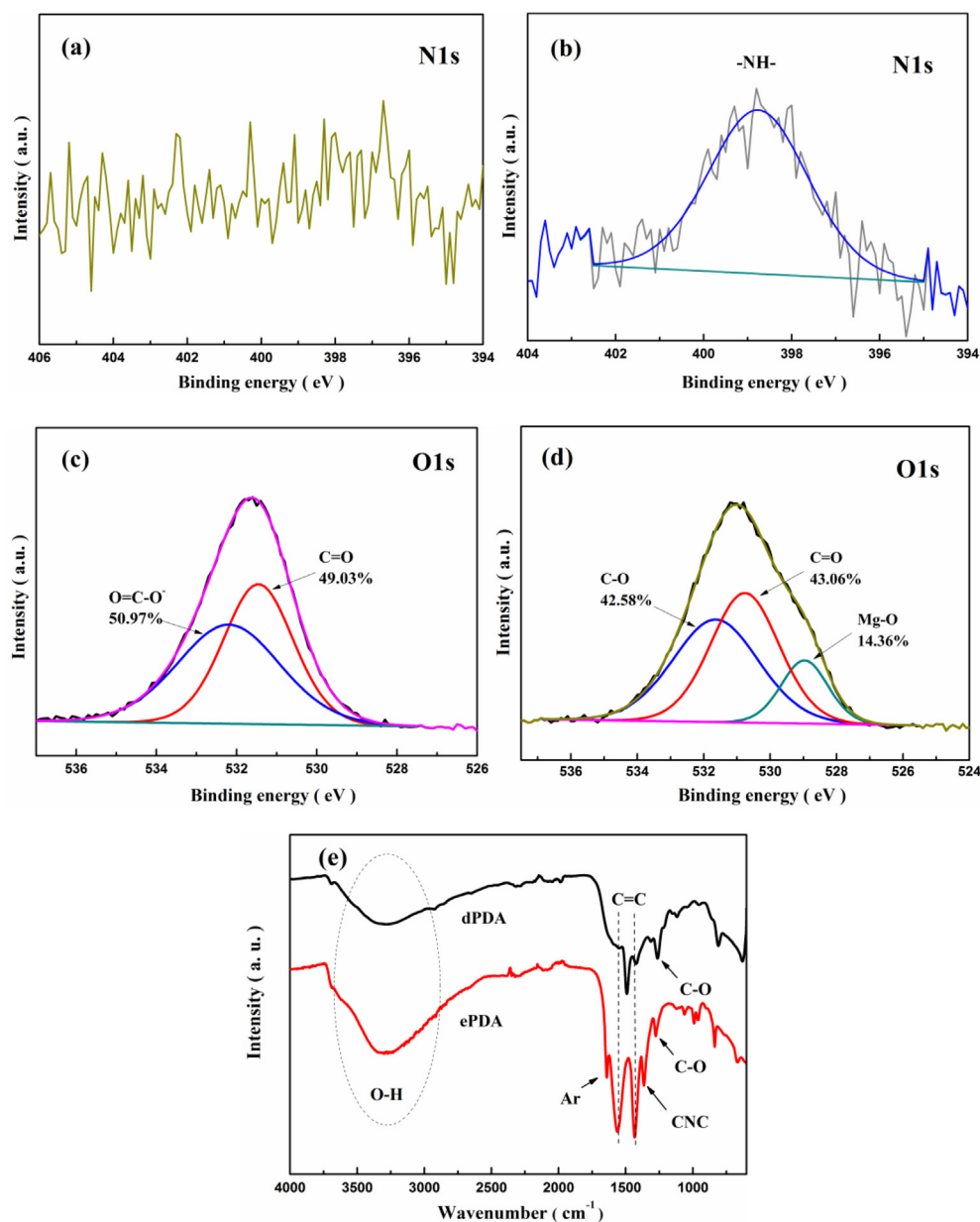


Fig. 1. High-resolution N1s patterns of (a) ePDA and (b) ePDA*; high-resolution O1s patterns of (c) ePDA and (d) ePDA*; (e) ATR-IR spectrum of dPDA (black) and ePDA (red).

not found in the ePDA sample [7], suggesting the different ways of DA electropolymerization and self-polymerization.

To control the electrochemical behavior of the Mg-Zn-Y-Nd alloy, the Mg alloy is polarized in 1 M SS solution (Fig. 2a). The first oxidation peak (-0.75 V) indicates that the anodic dissolution of electrode is inhibited by SS, while the second oxidation peak (0.65 V) results from the oxidation of SS [11]. Furthermore, according to Supporting information 7 and the literatures reported previously [6,12], it is known that the oxidation reaction of DA could occur in -0.5 V $\sim$ 0.6 V. Therefore, these results provide a possibility for DA to electropolymerize after passivation of the electrode and prior to the oxidation of SS. Fig. 2b presents the chronopotentiometric curve obtained from the preparation of ePDA. The potential increases sharply at the beginning and the working electrode occurs anodic dissolution. As time prolonged, a peak appears resulted from the passivation of the substrates by SS. Then, the ePDA film grows and ensures the stabilization of the potential on a bearing.

In comparison with dPDA (Fig. 2c), AFM image of ePDA (Fig. 2d) has a continuous structure and the surface roughness (RMS) is 13.0 nm, which is lower than that of dPDA (31.1 nm). As seen in Fig. 3a–b, unlike the rough surface of the dPDA coating, a relatively flatter ePDA film covers the whole surface of Mg alloy (Fig. 3b). The ePDA film thickness measured by spectroscopic ellipsometry is about 92 nm, which is far less than that of dPDA coating reported in the literature [7]. These are mainly due to the high electropolymerization rate of DA, which alleviates the substrates corrosion in solution.

To investigate the impact of different PDA layers on the properties of composite coating, we prepared PLLA coatings on Mg, dPDA and ePDA samples. As shown in Fig. 3c, d, the dPDA/PLLA coating surface has masses of noncontinuous ridges, while that of ePDA/PLLA is much flatter and has no obvious flaw. The results suggest

that the smooth ePDA film surface could induce a more uniform PLLA coating. Additionally, the layer thickness (Fig. 3e, f) were found to be approximately $8\text{ }\mu\text{m}$ and $3.1\text{ }\mu\text{m}$ for dPDA/PLLA and ePDA/PLLA samples, respectively. In accordance with the ASTM D3559-09, the ePDA/PLLA film adhesion was rated 5B, showing better adhesion compared with PLLA coating [13], which might be connected to the hydrogen bond between ePDA and PLLA.

From EIS (Fig. 3h), it could be seen that the ePDA/PLLA sample shows a significant increase of the charge transfer resistance, inductive resistance and inductance as compared to other coatings. In polarization curves (Fig. 3i–j), although the ePDA sample does not increase the corrosion resistance obviously, the ePDA/PLLA coating exhibits lower corrosion rate (4.407×10^{-7} A/cm²) compared with PLLA (2.308×10^{-6} A/cm²) and dPDA/PLLA coating (2.419×10^{-6} A/cm²). The mechanism for this phenomenon is that the insulativity of ePDA film hinders the transfer of electrons, and the compactness of ePDA/PLLA prohibited the penetration of corrosive ions [4]. In addition, the cathodic polarization current of the hydrogen evolution reaction on the ePDA/PLLA sample is lower than that on other samples which may be due to the uniform surface and the excellent adhesion strength. Accordingly, it could be concluded that ePDA film could provide better secondary modification effect compared with dPDA coating.

4. Conclusions

In this study, ePDA film on Mg-Zn-Y-Nd alloy was successfully achieved in SS aqueous solution. The ePDA film is a kind of salicylate and magnesium ions doped film. The smooth surface of ePDA film could induce a higher homogeneity PLLA layer than traditional dPDA coating and thus shows a better corrosion protection. Adhesion test shows ePDA film could improve the adhesion between

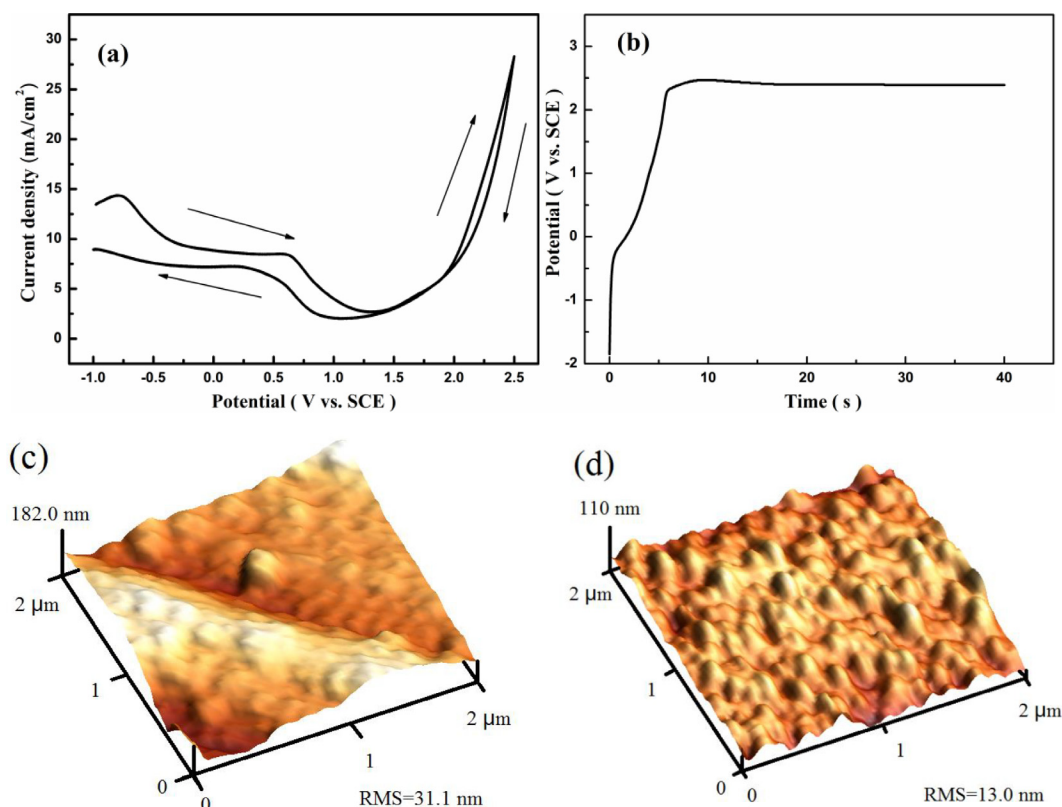


Fig. 2. (a). Voltammetric curve of Mg-Zn-Y-Nd alloy in 1 M SS solution, 20 mV/s. (b) potential-time curves for electropolymerization of dopamine on Mg-Zn-Y-Nd alloy in SS; AFM image of (c) dPDA and (d) ePDA.

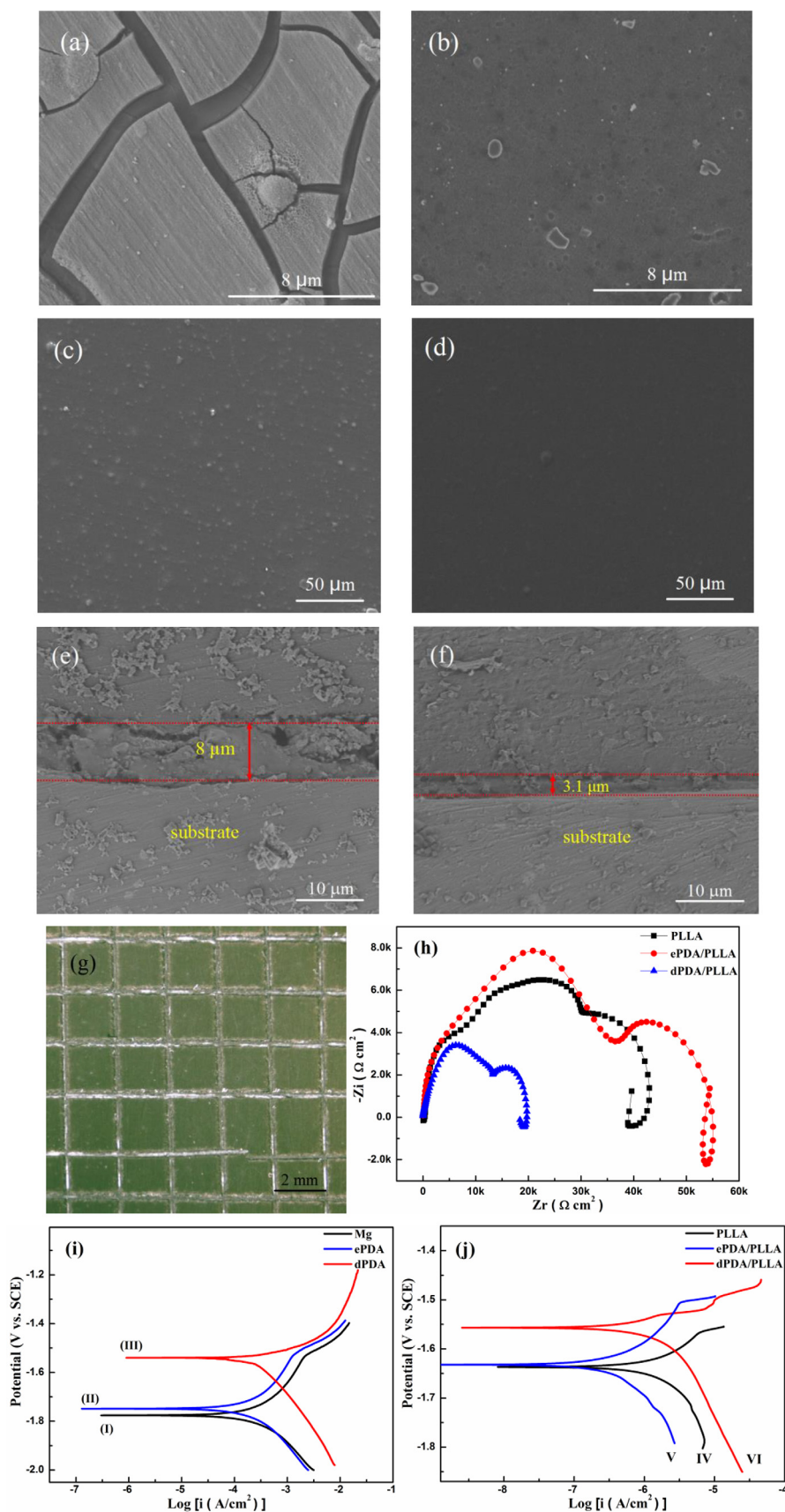


Fig. 3. SEM images of the surface morphology of (a) dPDA, (b) ePDA, (c) dPDA/PLLA and (d) ePDA/PLLA; cross-section SEM morphology of (e) dPDA/PLLA and (f) ePDA/PLLA; (g) macroscopic picture of ePDA/PLLA after adhesion test; (h) Nyquist EIS spectra, (i)–(j) Polarization curves in SBF of (I) Mg, (II) ePDA, (III) dPDA, (IV) PLLA, (V) ePDA/PLLA and (VI) dPDA/PLLA samples.

PLLA and Mg. This study suggested the ePDA film may provide a new insight into the surface modification of Mg alloys by DA since such ePDA film have a high potential for subsequent modification.

Conflict of interest

The authors declare no competing financial interest.

Acknowledgements

We are grateful for the financial support of National Natural Science Foundation of China (Grant No: 51671175), the National Key Research and Development Program of China (2017YFB0702504).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2019.04.122>.

References

- [1] Y.F. Zheng, X.N. Gu, F. Witte, *Mater. Sci. Eng. R: Reports* 77 (2014) 1–34.
- [2] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, *Science* 318 (5849) (2007) 426–430.
- [3] C. Wang, J. Shen, F. Xie, B. Duan, X. Xie, *Corros. Sci.* 122 (2017) 32–40.
- [4] Y. Chen, S. Zhao, M. Chen, W. Zhang, J. Mao, Y. Zhao, M.F. Maitz, N. Huang, G. Wan, *Corros. Sci.* 96 (2015) 67–73.
- [5] L. Guo, W. Wu, Y. Zhou, F. Zhang, R. Zeng, J. Zeng, *J. Mater. Sci. Tech* 34 (9) (2018) 1455–1466.
- [6] J.L. Wang, B.C. Li, Z.J. Li, K.F. Ren, L.J. Jin, S.M. Zhang, H. Chang, Y.X. Sun, J. Ji, *Biomaterials* 35 (27) (2014) 7679–7689.
- [7] F. Singer, M. Schlesak, C. Mebert, S. Hohn, S. Virtanen, *A.C.S. Appl. Mater. Interfaces* 7 (48) (2015) 26758–26766.
- [8] A. GhavamiNejad, L.E. Aguilar, R.B. Ambade, S.-H. Lee, C.H. Park, C.S. Kim, *Colloids Interf. Sci. Commun.* 6 (2015) 5–8.
- [9] M.C. Turhan, M. Weiser, H. Jha, S. Virtanen, *Electrochim. Acta* 56 (15) (2011) 5347–5354.
- [10] J. Petitjean, S. Aeiyaach, J.C. Lacroix, P.C. Lacaze, *J. Electroanal. Chem.* 478 (1–2) (1999) 92–100.
- [11] M.B. González, S.B. Saidman, *Electrochem. Commun.* 13 (5) (2011) 513–516.
- [12] Y. Li, M. Liu, C. Xiang, Q. Xie, S. Yao, *Thin Solid Films* 497 (1–2) (2006) 270–278.
- [13] F. Singer, T. Distler, S. Virtanen, *Int. J. Electrochem. Sci.* 9 (2014) 7965–7976.