

Short Communication

Electrochemical Corrosion Behaviour of Cerium Chemical Conversion Coatings on 304 Stainless Steel in Alkaline Solutions Containing Chloride Ions

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A chemical conversion coating was successfully prepared on the surface of 304 stainless steel (SS). The morphology and chemical composition of the obtained coating were analysed by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). The electrochemical corrosion behaviour was investigated in 3.5 wt.% NaCl with different pH values. The results show that the chemical conversion coating is quite stable in alkaline solutions containing chloride ions. The coated 304 SS shows much higher corrosion potential and pitting potential in comparison with the uncoated 304 SS. It is suggested that the chemical conversion coating can noticeably improve the pitting corrosion resistance of 304 SS. In addition, the cerium chemical conversion coating shows good pitting resistance in an alkaline solution with increasing pH values.

Keywords: Stainless steel; Chemical conversion; Coating; Corrosion; Rare earth;

1. INTRODUCTION

Corrosion control is one of the most important topics of metals, due to the enormous cost (over 3% of the world's GDP) caused by corrosion failure [1, 2]. To date, metal corrosion can be controlled via various approaches, such as cathodic protection and passivation along with the use of coatings and corrosion inhibitors [3-7]. Stainless steels, which usually show good corrosion resistance owing to protective passive films that form on the surface, have been widely investigated in the past few decades [8-10]. However, the corrosion resistance and stability of passive films formed on stainless steels have shown to be hindered by some species such as Cl^- , S^{2-} , and $\text{S}_2\text{O}_3^{2-}$ [11-13]. To alleviate the adverse influences of aggressive ions, surface treatment technologies such as chemical conversion coating are often employed to further improve the corrosion resistance of stainless steels [14-16].

Chromate-based conversion coatings have been widely adopted to provide excellent corrosion resistance for carbon steel, magnesium alloy and stainless steel [17]. Unfortunately, their application is hindered by the biological toxicity and environmental damage caused by hexavalent chromium [18, 19]. Therefore, tremendous work has been devoted to exploring and developing the eco-friendly conversion coatings with acceptable corrosion resistance to replace traditional chromate conversion coatings [20].

Currently, molybdate, phosphate, zirconium and rare earth conversion coatings have been proposed as candidates for non-chromate conversion coatings [21-24], of which the cerium chemical conversion coating shows effective protection for stainless steels (e.g., 316L, 304, etc.) [14, 25]. However, studies of the corrosion behaviour of cerium chemical conversion coatings on stainless steel in alkaline solutions (such as concrete and secondary side environments [16, 26-29]) are relatively rare. In this paper, a cerium chemical conversion coating was successfully prepared on 304 stainless steel and the electrochemical behaviour of this conversion coating was investigated in alkaline solutions containing chloride ions. It is anticipated that this research will provide an eco-friendly conversion coating for stainless steels used in alkaline environments.

2. EXPERIMENTAL

Commercial 304 stainless steel was used as the substrate. The specimens (10 mm×10 mm×5 mm) were prepared by electrical discharge machining followed by grinding and polishing. Then the specimens were degreased in alcohol, washed in distilled water and dried in air. After that, the specimens were immersed in treatment solutions for the preparation of cerium chemical conversion coatings according to the literature [14]. The composition of the treatment bath and the operating parameters are listed in Table 1.

Table 1. The bath solution composition and operating parameters for cerium chemical treatment.

Composition		Operating parameter
Ce(NO ₃) ₃ ·6H ₂ O	9.98 g L ⁻¹	Temperature: 70 °C
C ₆ H ₈ O ₇	5.88 g L ⁻¹	
H ₂ O ₂ (30%)	660 mL L ⁻¹	Time :30 min

The morphologies and chemical composition of the samples were investigated using scanning-electron microscopy (SEM, Zeiss Sigma 500) in conjunction with an energy-dispersive spectrometry (EDS, Oxford) operating at 15 kV.

The electrochemical measurements were conducted using a Parstat VersaSTAT 3F workstation (Princeton Application Research) with a conventional three-electrode electrochemical cell, consisting of the specimen as the working electrode, a Pt sheet (20 mm × 20 mm) as the counter electrode, and a saturated-calomel electrode (SCE) as the reference electrode. Prior to electrochemical tests, the specimens were mounted in epoxy resin, leaving a working area of 1 cm². The test solution was 3.5 wt.% NaCl with different pH values (8, 9, 10, 11 and 12). The pH value was adjusted by using a dilute

NaOH solution. The anodic polarization curves were performed at 25 °C using a scan rate of 10 mV min⁻¹ that started from -0.05 V vs. the corrosion potential (E_{corr}) until the current density reached 1 mA cm⁻². All the solutions used in the experiments were prepared by analytical grade chemicals and deionized water.

3. RESULTS AND DISCUSSION

After cerium chemical treatment, the surface of the 304 SS specimen transforms to a bright golden yellow, which is a typical characteristic of a cerium chemical conversion coating. Fig. 1 shows the morphology and the EDS mapping of the obtained coating.

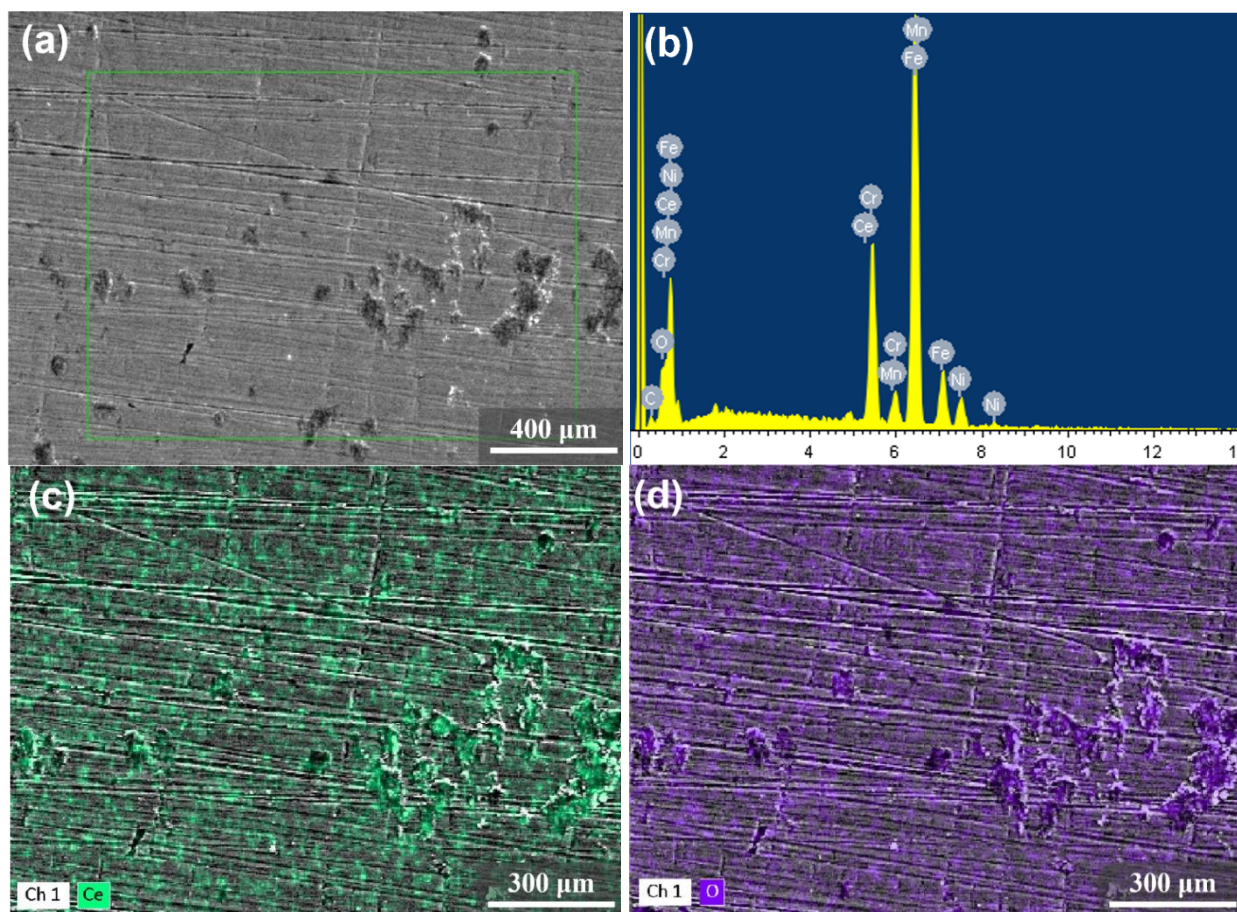


Figure 1. The surface morphology (a) and EDS spectrum (b) of the obtained cerium chemical conversion coating on 304 SS and the EDS mapping for the Ce (c) and O (d) elements.

As shown in Fig. 1(a), it is hard to observe the thin conversion coating except for some small deposits. However, Fe, Cr, Ni, Mn, Ce and O elements are clearly visible in the EDS spectrum of the surface (Fig. 1(b)), of which the Fe, Cr, Ni and Mn elements should be attributed to the 304 SS substrate. The Ce and O elements in the EDS spectrum can confirm the formation of cerium chemical conversion coating on the surface of the 304 SS specimens. In addition, the EDS mapping in Fig. 1(c-

d) shows that the Ce and O elements are distributed on the whole surface and form some small oxide islands. This visual observation is similar to the cerium chemical conversion coating on 316L SS [14], revealing that a compact and homogeneous cerium chemical conversion coating was successfully deposited on the surface of the 304 SS specimen.

Fig. 2 displays the E_{corr} vs. time curves for the coated and uncoated 304 SS specimens in the test solutions with different pH values. It can be found that the E_{corr} for each specimen finally tends to reach a steady-state after 2 h of immersion. The stable E_{corr} values of uncoated 304 SS became more negative as the pH value of the electrolyte increased. This is similar to the results of the AISI 304 SS and 316L SS in the alkaline solutions containing chloride ions. The reason is that the OH^- and Cl^- ions may modify the composition of the passive films on the stainless steel surface, and the Cr(III) and Fe(III) species decrease in the passive films as the Fe(II) and Ni species increase as the pH increases [30-32]. Similarly, the stable E_{corr} value of coated 304 SS decreases with the increase in pH value of the electrolyte, demonstrating that the electrochemical response of the cerium chemical conversion coating is also affected by the electrolyte pH. In addition, Fig. 2 shows that the E_{corr} values of coated 304 SS specimens are much higher than those of the uncoated 304 SS specimens, indicating that the cerium chemical conversion coating can provide protection for 304 SS and reduce corrosion susceptibility in these solutions [33, 34].

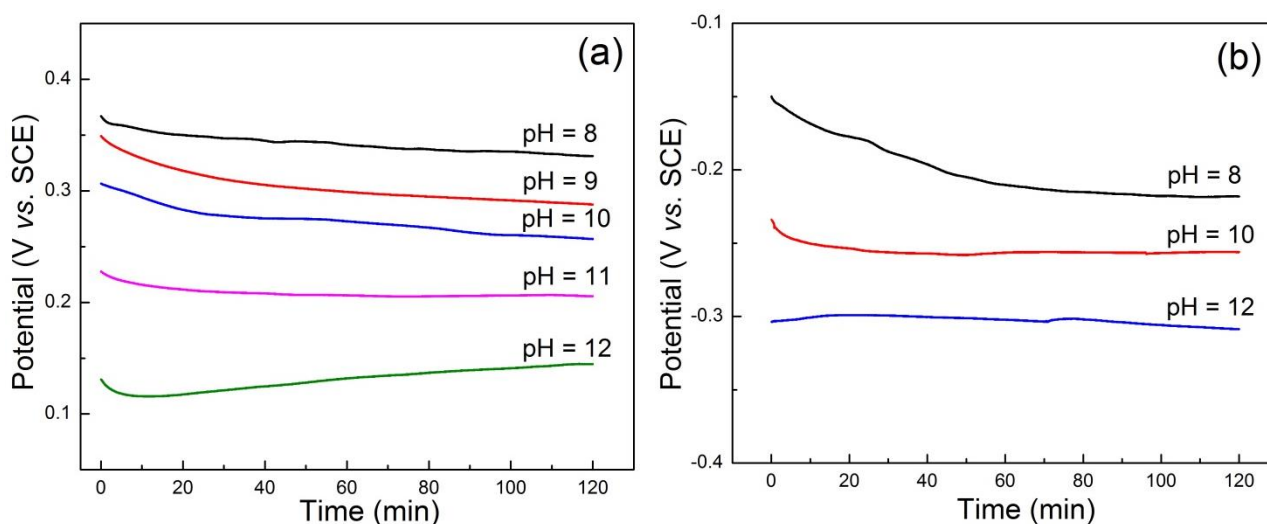


Figure 2. Variation in corrosion potential with time for (a) coated and (b) uncoated 304 SS specimens in 3.5 wt.% NaCl solutions with different pH values at 25 °C.

Fig. 3 shows the anodic polarization curves of the coated and uncoated 304 SS specimens. As shown in Fig. 3(b), the passive current density (i_{pass}) increases, and the pitting potentials (E_{pit}) shift to much higher values as the pH increases. The austenitic stainless steels (AISI 304, 316) have similar behaviour in the literature [30, 31]. These behaviours can be attributed to the varying compositions of the passive films and the inhibition of pit formation and propagation under high alkaline pH conditions induced by the dissolution of the MnS inclusions and relevant local acidification [30, 31].

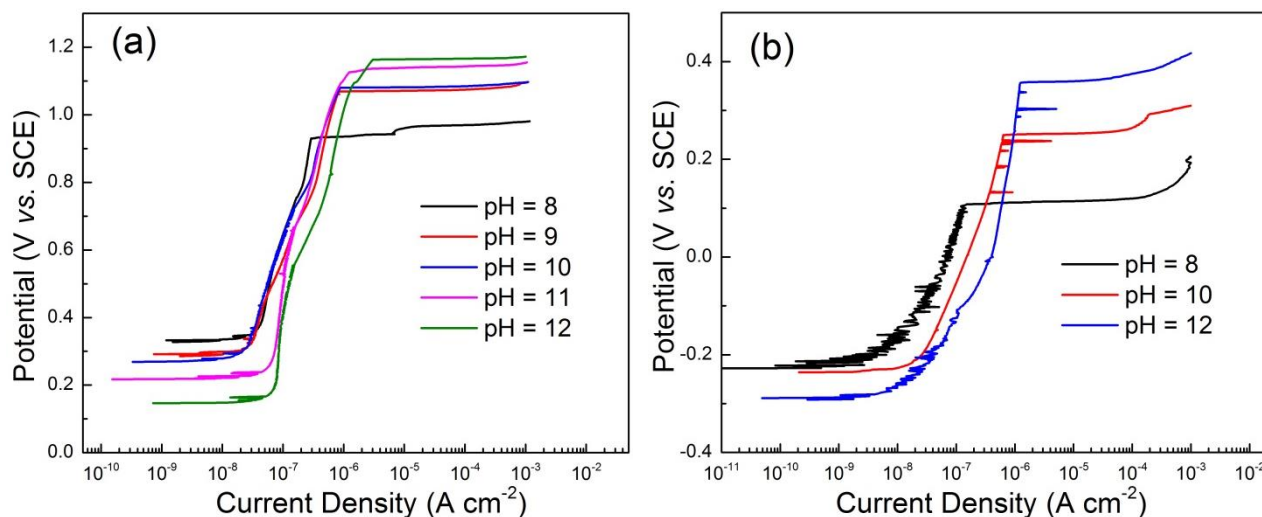


Figure 3. Anodic polarization curves of the (a) coated and (b) uncoated 304 SS specimens in 3.5 wt.% NaCl solutions with different pH values at 25 °C.

According to the much high E_{corr} and E_{pit} values in conjunction with an enormously wide passivation region (Table 2) [35], the coated 304 SS specimens display tremendous improvement in the resistance to pitting corrosion compared that of uncoated specimens. The protection of the cerium chemical conversion coating for 304 SS can also be confirmed by the morphologies of the pits on the coated and uncoated 304 SS surfaces after the anodic polarization measurements in Fig. 4. Apparently, the pits on the uncoated 304 SS specimen are much deeper than those on the coated ones. In addition, it should be noted that the pit mouth is smaller than the pit interior for the uncoated 304 SS specimens, resulting in stable growth within the occluded pit. The pits on the coated 304 SS specimens are fully open without any cover, thus, repassivation is possible instead of just stable growth [14, 36]. In addition, as presented in Fig. 3(a), the E_{pit} value of the coated 304 SS specimen increases and the passivation region becomes wider with increasing pH. These observations may be the result of the higher stability of insoluble cerium oxide species in a more alkaline pH solution according to the Pourbaix diagram [37-39]. Therefore, it can be concluded that the cerium chemical conversion coating would exhibit good pitting corrosion resistance in a more alkaline pH solution with 3.5 wt.% NaCl.

Table 2. The electrochemical parameters extracted from Figs. 3 and 4.

Sample	Coated					Uncoated			
	pH	8	9	10	11	12	8	10	12
E_{corr} (mV vs. SCE)		332	288	254	205	144	-218	-256	-308
E_{pit} (mV vs. SCE)		929	1067	1079	1124	1162	109	251	355
$E_{\text{pit}} - E_{\text{corr}}$ (mV)		597	779	825	919	1018	327	507	663

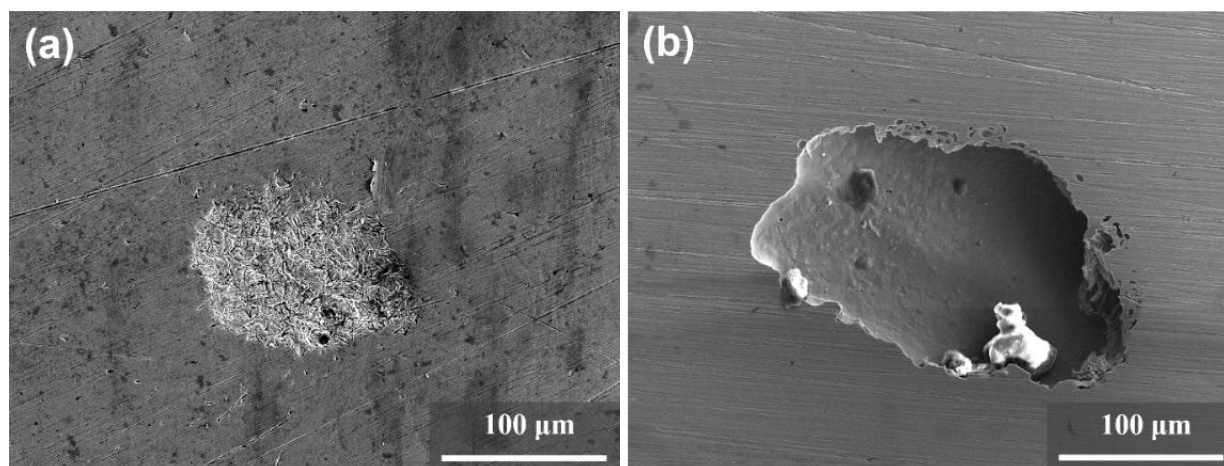


Figure 4. The typical surface morphologies of the pits on the (a) coated and (b) uncoated 304 SS specimens after the anodic polarization measurements in a 3.5 wt.% NaCl solution (pH = 10).

4. CONCLUSIONS

In this study, a compact and homogeneous cerium chemical conversion coating was successfully prepared on the surface of 304 SS. The chemical conversion coating is stable in alkaline solutions containing chloride ions, which may greatly increase the E_{corr} and E_{pit} values of 304 SS. The pits on the uncoated 304 SS are much deeper than those on the coated ones. It can be concluded that the chemical conversion coating improves the pitting corrosion resistance of 304 SS in alkaline solutions containing chloride ions. The cerium chemical conversion coating shows good pitting corrosion resistance with increasing pH values from 8 to 12 in a 3.5 wt.% NaCl solution.

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References

1. S. Ding, T. Xiang, C. Li, S. Zheng, J. Wang, M. Zhang, C. Dong, W. Chan, *Mater. Des.* 117 (2017) 280.
2. Q. Zhou, S. Sheikh, P. Ou, D. Chen, Q. Hu, and S. Guo, *Electrochem. Commun.*, 98 (2019) 63.
3. Y. F. Zhu, R. G. Du, W. Chen, H. Q. Qi, C. J. Lin, *Electrochem. Commun.*, 12(2010) 1626.
4. Q. Zhou, J. Jiang, Q. Zhong, Y. Wang, K. Li and H. Liu, *J. Alloy. Compd.*, 563 (2013) 171.
5. S. V. Lamaka, D. Höche, R. P. Petrauskas, C. Blawert, M. L. Zheludkevich, *Electrochem. Commun.*, 62 (2016) 5.
6. Q. Zhou, S. Liu, L. Gan, X. Leng, S. Wei, *Mater. Res. Express.*, 5 (2018) 116534.
7. X. Leng, Y. Zhang, Q. Zhou, Y. Zhang, Z. Wang, H. Wang and B. Yang, *Mater. Res. Express.*, 5 (2018) 056513
8. S. S. Xin, M. C. Li, *Corros. Sci.*, 81 (2014) 96.
9. H. Yan, S. Xin, Y. Yang, S. Yang, M. Li, *Int. J. Electrochem. Sc.*, 14 (2019) 1423.

10. C. Liu, M. Gong, X. Zheng, *Int. J. Electrochem. Sc.*, 13 (2018) 7432.
11. X. Cheng, Y. Wang, C. Dong, X. Li, *Corros. Sci.*, 134 (2018) 122.
12. L. Choudhary, D. D. Macdonald, A. Alfantazi, *Corrosion*, 71 (2015) 1147.
13. Z. Wang, L. Zhang, Z. Zhang, M. Lu, *Appl. Surf. Sci.*, 458 (2018) 686.
14. J. Xu, S. S. Xin, P. H. Han, R. Y. Ma, M. C. Li, *Mater. Corros.*, 64 (2013) 619.
15. F. Mansfeld, C. B. Breslin, A. Pardo, F. J. Perez, *Surf. Coat. Tech.*, 90 (1997) 224.
16. J. Liu, C. Wang, W. Zhang, T. Xia, X. Zhang, T. Liang, T. Ahmad, B. Yang, *Mater. Sci. Tech.* (2019) 1-9.
17. M. W. Kendig, R. G. Buchheit, *Corrosion*, 59 (2003) 379.
18. B. Ramezanzadeh, H. Vakili, R. Amini, *J. Ind. Eng. Chem.*, 30 (2015) 225-233.
19. Z. M. Al-Rashidy, M. M. Farag, N. A. Ghany, A. M. Ibrahim, W. I. Abdel-Fattah, *Surf. Coat. Tech.*, 334 (2018) 47.
20. S. M. Cohen. *Corrosion*, 51(1995): 71.
21. B. Liu, X. Zhang, G. Y. Xiao, Y. P. Lu, *Mat. Sci. Eng. C*, 47 (2015) 97.
22. J. Mondal, A. Marques, L. Aarik, J. Kozlova, A. Simões, V. Sammelseg, *Corros. Sci.*, 105 (2016) 161.
23. H. R. Asemani, A. A. Sarabi, H. E. Mohammadloo, M. Sarayloo, *J. Coat. Technol. Res.*, 13 (2016) 883.
24. U. Eduok, J. Szpunar, *Ultrason. Sonochem.*, 44 (2018) 2888.
25. C. Wang, F. Jiang, F. Wang, *Corros. Sci.*, 46 (2004) 75.
26. H. Luo, C. F. Dong, X. G. Li, K. Xiao, *Electrochim. Acta*, 64 (2012) 211.
27. J. Wang, J. Wang, *J. Mater. Sci. Technol.*, 31 (2015) 1039.
28. G. D. Song, W. I. Choi, S. H. Jeon, J. G. Kim, D. H. Hur, *J. Nucl. Mater.*, 512(2018) 8.
29. S. Li, Y. Wang, H. Wang, C. Xin, X. Wang, *J. Nucl. Mater.*, 469 (2016) 262.
30. L. Freire, M. J. Carmezim, M. G. S. Ferreira, M. F. Montemor, *Electrochim. Acta*, 56(2011) 5280.
31. L. Freire, M. J. Carmezim, M. G. S. Ferreira, M. F. Montemor, *Electrochim. Acta*, 55(2010) 6174.
32. L. Freire, M. A. Catarino, M. I. Godinho, M. J. Ferreira, M. G. S. Ferreira, A. M. P. Simões, M. F. Montemor, *Cement. Concrete. Comp.*, 34 (2012) 1075.
33. W. Liu, Q. Xu, J. Han, X. Chen, Y. Min, *Corros. Sci.* 110 (2016) 105-113.
34. T. J. Pan, Y. Chen, B. Zhang, J. Hu, C. Li, *Appl. Surf. Sci.*, 369 (2016) 320.
35. A. L. Rudd, C. B. Breslin, F. Mansfeld, *Corros. Sci.* 42(2000) 275.
36. P. Ernst, N. J. Laycock, M. H. Moayed, R. C. Newman, *Corros. Sci.* 39 (1997) 1133.
37. S. A. Hayes, P. Yu, T. J. O'Keefe, M. J. O'Keefe, J. O. Stoffer, *J. Electrochem. Soc.*, 149(2002) C623.
38. P. Yu, S. A. Hayes, T. J. O'Keefe, M. J. O'Keefe, J. O. Stoffer, *J. Electrochem. Soc.*, 153(2006) C74.
39. P. Yu, T. J. O'Keefe, *J. Electrochem. Soc.*, 153(2006) C80.