

Influence of PANI and Magnesium Particles coating on Aluminium Alloy (5083) Corrosion in 3.5 % Sodium Chloride Solution

Xiangyu Lu¹, Zhanqing Qu¹, Xuesen Zhang², Bo Wang^{3,*}, Shuai Qu⁴, Xingguo Feng¹, Zheng Chen^{5,*}

¹ College of Harbour, Coastal and Offshore Engineering, Hohai University, Nanjing 210098 Jiangsu, China

² CGN New Holdings Co.,Ltd., Beijing, 100071, China

³ Marine Chemical Research Institute, State Key Laboratory of Marine Coatings, Qingdao, 266072, China

⁴ AVIC BIAM New Materials Technology & Engineering Co., Ltd, Beijing, 100095, China

⁵ Guangxi Key Laboratory of Disaster Prevention and Engineering Safety, Guangxi University, Nanning 530004, People's Republic of China

*E-mail: wangbo@haohua.chemchina.com, chenzheng@gxu.edu.cn

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Polyaniline (PANI) particles were added in Mg-rich primer (MRP) on 5083 aluminum alloy and enhanced the protective performance of MRP greatly. The coating performance was studied with Machu test, OCP, EIS and SEM. The results showed that the optimal PANI particles is 1 wt%. Firstly, the PANI particles with a proper content improved the electrical contact of Mg particles and 5083 substrate, leading to the enhancement of the cathodic protection. Secondly, the PANI particles could improve the compactness of the products of Mg particles, improving barrier effects of the coating. Finally, the PANI particles could retard the reaction activities of the Mg particles in coatings, thereby reducing their consumption rate.

Keywords: Aluminum alloy; Mg-rich primer; Polyaniline; EIS

1. INTRODUCTION

Aluminum alloys have been widely used in ships and marine equipment due to their low density, high strength, weldability, easy processing and forming, non-magnetic, and good low temperature performance. The application of aluminum alloys is an important measure to reduce hull quality, improve sailing speed, and reduce operating energy consumption [1, 2]. In the marine environment, chloride ions can easily induce the rupture of oxide film on the surface of aluminum alloy, leading to pitting corrosion,

gap corrosion, intergranular corrosion, exfoliation corrosion, stress corrosion cracking and other forms of corrosion failure [3]. Compared with other corrosion protective technologies, organic coatings have low cost, simple process and excellent corrosion protective performance, and are widely used in marine equipment protection [4, 5]. In the process of long-term service, organic coatings will inevitably be damaged and cracked due to environmental aging and external damage, resulting in substrate corrosion at coating defects and accelerated coating failure [6]. Therefore, it is necessary to improve the damage resistance of the coating and reduce the adverse effect of the coating defect on its protection performance.

In recent years, Mg-rich epoxy coatings have been developed rapidly with adding pure magnesium particles into epoxy coatings to provide cathodic protection for aluminum alloys [7-16]. The results show that the protection of Mg-rich coatings on aluminum alloys can be divided into two stages: the Mg-rich coatings provide mainly cathodic protection in the early stage; in the later stage, the corrosion products of Mg particles present barrier effect [15,16]. Although Mg-rich coatings can provide multiple protections for aluminum alloys matrix, their cathodic protection failed rapidly resulting from the high reactivity of Mg particles [17]. In addition, the initial reaction of Mg particles is fast and releases a large amount of hydrogen, leading to that the coating is prone to bubble and other defects [18-23]. Meanwhile, the structure of corrosion products for Mg particles is relatively loose its so the barrier effect of MRPs is limited after the cathodic protection of pure Mg fails [18-23].

Polyaniline (PANI) is widely used in corrosion protective coatings because of its good conductivity, easy preparation, stability and non-pollution. The protective performance of the epoxy coatings on aluminum alloys were significantly improved with addition of appropriate polyaniline[24-28]. Both the doped ions released by polyaniline and the oxidation-reduction reaction of polyaniline can promote the formation of a protective layer on the aluminum alloy substrate at the coating defects, so that the organic coatings containing polyaniline have a certain self-healing function [24-28]. In addition, it was found that HF-doped polyaniline in the epoxy coating can capture chloride ions to slow down the diffusion of corrosive media in the coating, and also form a protective film on the surface of the AZ91D alloy to delay the corrosion expansion of the substrate [22]. Therefore, polyaniline was added in Mg-rich epoxy coatings on aluminum alloys to improve their protective performance in this paper.

2. EXPERIMENTAL METHODS

2.1. Materials

AZ91D alloy sheets were provided by Qiyue metal materials Co., Ltd, China. Table 1 displayed the chemical compositions.

Shijiazhuang Golden Fish Paint Company (China) supplied the two component commercial epoxy (KFH-01) used in this paper . Pure Mg particles (99.9%), with the average diameter size of 5–10 μm , were adopted and produced by Tangshan Weihao Magnesium Powder Co., Ltd (Tangshan Hebei, China). The coupling agent was a γ -glycidoxy propyl trimethoxy silane (γ -GPS) supplied by Jinhong Rubber Industry Co., Ltd (China). Emeraldine base PANI was purchased from Cool Chemical Technology (Beijing) co. Ltd.

Table 1. Nominal composition (wt.%) of 5083 aluminium alloy

Mg	Mn	Cr	Fe	Ti	Cu	Al
4.5	0.5	0.20	0.3	0.10	0.08	remainder

2.2. Sample preparation

5083 aluminium alloy coupons with dimensions of 50 mm × 50 mm × 3 mm were cut from the commercial sheet and were ground to 240 grit. Prior to be coated, the samples were rinsed with distilled water, degreased in ethanol and acetone in turn, then dried in air.

The Mg-rich primers (MRPs) with varying PANI were prepared by adding pure magnesium particles and PANI powders into the epoxy paint. The different coatings are labeled as tabulated in Table 2. The γ -GPS coupling agent (1% w/w with respect to the pigment weight) was added in the primer as dispersing agent. A high speed agitation equipment was employed for dispersion of pigments. After dispersion for 10 min, the curing agent polyamide was added to the primer. The weight ratio of polyamide and epoxy was 3:10. Then the primer was applied to 5083 panels by brushing. The painted panels were kept indoors for 7 days before being tested. The thickness of the dry primer was about 130 μm ($\pm 10 \mu\text{m}$) which was measured with a coating thickness gauge EC776FN.

Table 2. PVC, Mg content on dry film and labels of different Mg-rich primers.

Label	PANI-HF content on dry film (%)	Mg content on dry film (%)
MRP	0	50
1% PANI-MRP	1	49
3% PANI-MRP	3	47
5% PANI-MRP	5	45

2.3. SEM

A Hitachi S4700 scanning electron microscope (SEM) was employed to observe the 5083 substrate. The samples were coated with gold to preclude the charging effect during measurement.

2.4. Machu test

Prior to Machu test, the coated samples were scribed on the surface with a razor blade. HY-914 resin was used to seal the edges of samples. The test solution was composed of 5% NaCl, 10% H₂O₂ and 10 ml/L acetic acid and the test temperature was 37 °C. After 24 h of immersion, another 10% H₂O₂ was supplemented in the test solution. Corrosion phenomena along the scratches were characterized by macro-observation after 48 h of immersion.

2.6. XPS

X-ray photoelectron spectroscopy (XPS) was utilized to characterize the surface compositions of the 5083 alloy after the coating was peeled off from the alloy substrate. XPS measurements were carried out with an ESCALAB 250 instrument, with a monochromatized Al K line (1486 eV) as the excitation source. All the binding energy values were calibrated according to C 1 s peak at 284.6 eV. The narrow scan spectra were fitted with XPSPEAK 4.1 software.

2.7. Electrochemical measurements

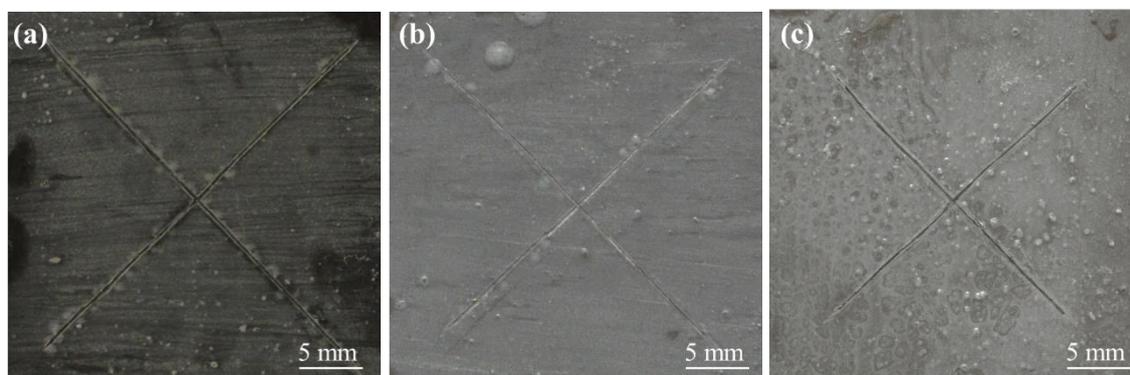
For the MRP coated samples, electrochemical impedance spectroscopy (EIS) experiments were performed in 3 wt.% NaCl solution with a AutoLab 302N system, over a frequency range of 100 kHz to 10 mHz, with a sinusoidal amplitude of 10 mV. The working area of coated samples was 10 cm². Similarly, the reference was a SCE and the counter electrode was a Pt mesh. ZSimpWin software was utilized to fit the impedance spectra. The open circuit potentials (OCP) of different coatings were measured before the EIS tests.

3. RESULTS AND DISCUSSION

3.1. Machu test

Figure 1 revealed the Machu test results for MRP and PANI-MRP coated samples. For the MRP coated sample (Fig. 1a), severe coating delamination and many tiny bubbles appeared along the scratches.

For the PANI-MRP coated samples (Fig. 1b, c and d), the coatings remained good adhesion without serious disbanding and the aluminium substrate at the scratches had a metallic luster (Fig. 1b), indicating that the protective performance of the MRP on 5083 alloy was obviously enhanced by the PANI particles.



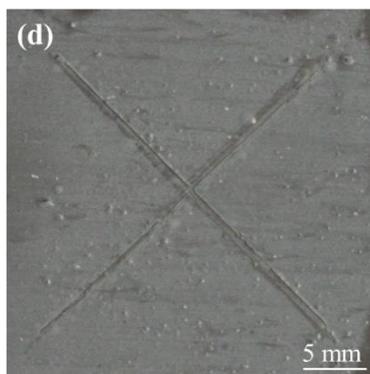


Figure 1. Machu testing results for scratched coating samples: (a) MRP sample; (b) MRP sample, coating removed; (c) SAP-PANI-MRP sample; (d) SAP-PANI-MRP sample, coating removed.

3.3. Open circuit potential (OCP)

Figure 2 presented the variations of the OCPs for the MRP and PANI -MRP samples with immersion time in the 3 wt% NaCl solution. In the entire immersion, the E_{OCP} of the MRP coated sample was below $-0.8 V_{SCE}$, the E_{OCP} for 5083 alloy substrate in 3 wt% NaCl solution, indicating that the MRP could protect the 5083 alloy cathodically. As immersion time prolonged, the E_{OCP} of the MRP sample increased because of the accumulation of $Mg(OH)_2$ in the micro-pores of coatings [15]. The E_{OCP} was PANI-SAP-MR coated sample below $-0.8 V_{SCE}$ during the whole immersion time, showing the same cathodic protection effect to MRP. The E_{OCP} of PANI-SAP-MR increased because of the formation of Mg particles corrosion products. In the immersion time from the initial to 336 hours, the E_{OCP} values of 1% PANI-MRP and 3% PANI-MRP were lower than those of MRP while their E_{OCP} values were higher than those of MRP in the following immersion.

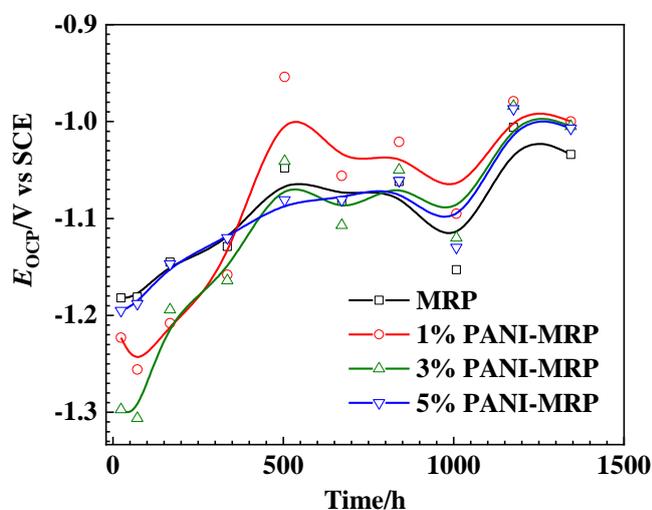
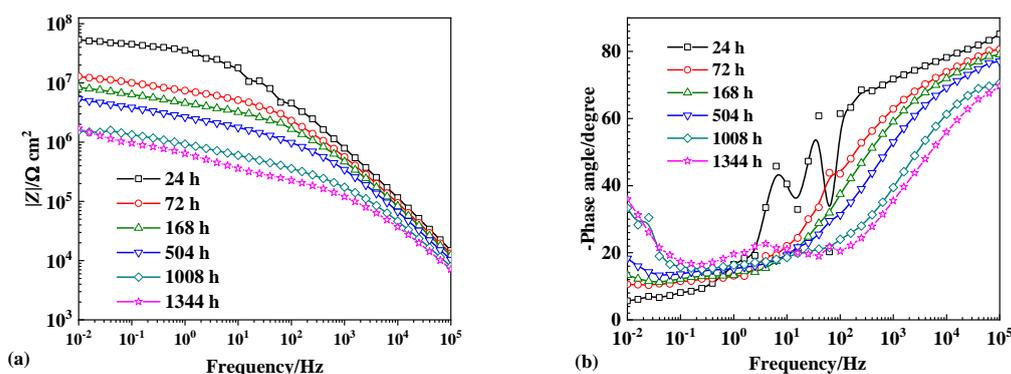


Figure 2. The variations of the open circuit potential for the MRP and PANI -MRP samples with immersion time in the 3 wt% NaCl solution.

This phenomenon may be explained by the effects of PANI particles on MRP [22]. In one hand, PANI particles could improve electrical contact between the Mg particles and the substrate, leading to an enhancement of the cathodic protection [22]. In the other hand, the products of the Mg particles in PANI-MRP were compact in compared to those in MRP precipitated on the particles, thereby improving the barrier effects of the coating [22].

3.4. EIS measurement

Figure 3 presents the bode plots of different MRP samples immersion in 3 wt% NaCl solution. The module of electrochemical impedance at 0.01 Hz ($|Z|_{0.01 \text{ Hz}}$) in the EIS is a measure of the protection performance for coatings [17-19]. For convenience, the variations of $|Z|_{0.01 \text{ Hz}}$ values for different coating samples as a function of immersion time is displayed in Fig. 4. For the MRP coated sample, $|Z|_{0.01 \text{ Hz}}$ exceeded $53 \text{ M}\Omega \text{ cm}^2$ after 1 day of immersion, indicating a classical barrier-type coating behavior. After 7 days of immersion, $|Z|_{0.01 \text{ Hz}}$ dropped to $8 \text{ M}\Omega \text{ cm}^2$, attributing to the electrolyte permeation into the coating and the activation of the Mg particles. As immersion time prolonged, $|Z|_{0.01 \text{ Hz}}$ showed an increase. This phenomenon was ascribed to formation of Mg particles corrosion products in coating, providing the barrier protection to some extent [17, 19, 21]. Thereafter, the $|Z|_{0.01 \text{ Hz}}$ value decreased slowly, reflecting that the protective performance of the MRP persisted without obvious deterioration. The trends of $|Z|_{0.01 \text{ Hz}}$ values for 1%PANI-HF/MRP, 3%PANI-HF/MRP and 5%PANI-HF/MRP coated samples were similar to that of MRP. However the $|Z|_{0.01 \text{ Hz}}$ values of 1%PANI-HF/MRP and 3%PANI-HF/MRP were higher than those of MRP while the $|Z|_{0.01 \text{ Hz}}$ values of 5%PANI-HF/MRP were lower than those of MRP. Hence it could be inferred that the PANI particles with appropriate content could enhance the stability of MRP, prolonging the coating lifetime, but high PANI addition was not beneficial for barrier effect. When the content of PANI particles were higher than 3%, many PANI-HF particles aggregate on the coating surface as the PANI concentration increases. As a consequence, the microdefects in coatings increase leading to a decrease of the coating barrier effects. This phenomenon resembles the effects of HF doped PANI for MRP on AZ91D alloy [22].



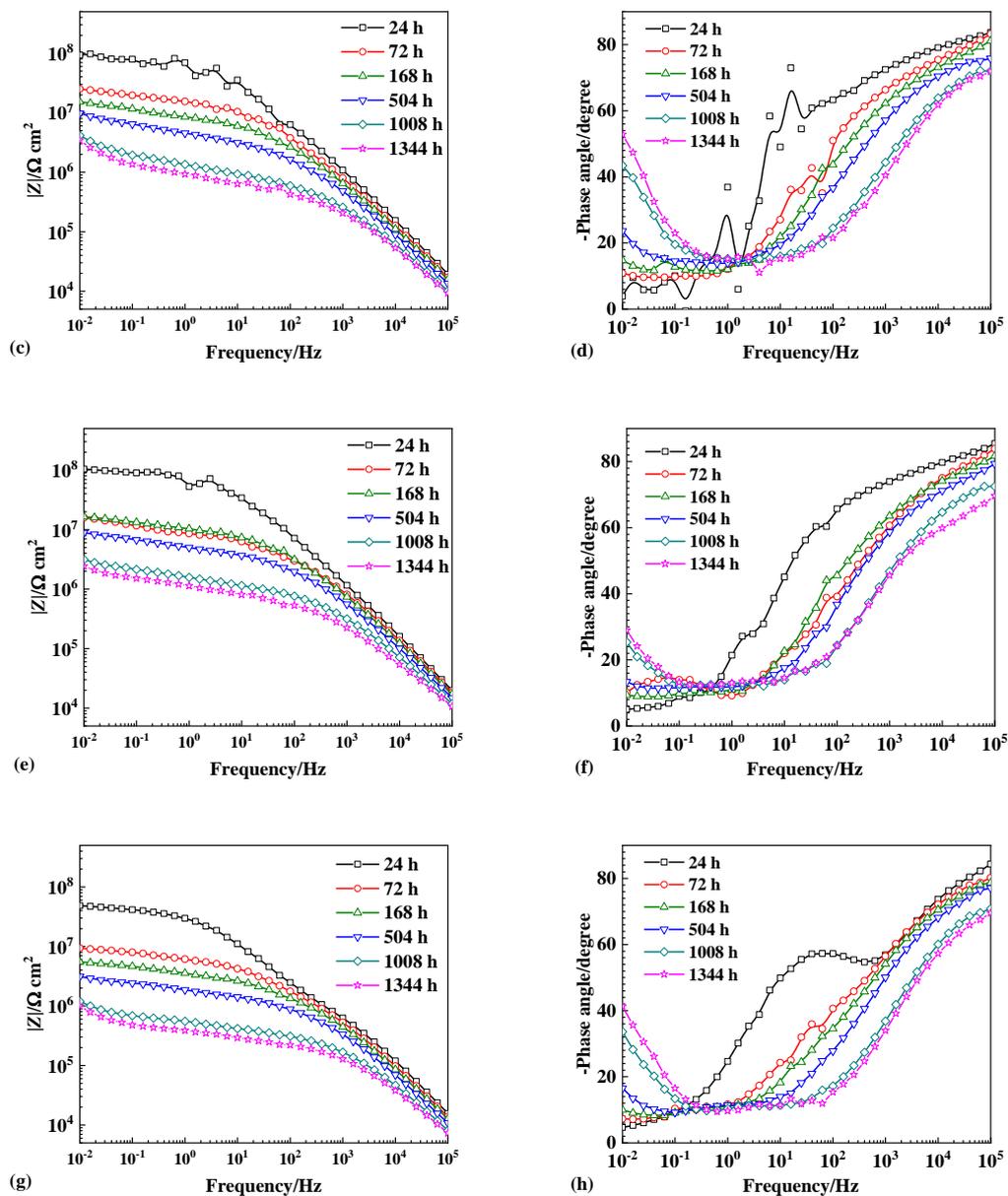


Figure 3. Bode plots of different MRP samples after immersion in 3.0 wt% NaCl solution for different days: a) and b) MRP; c) and d) 1%PANI -MRP; e) and f) 3%PANI- MRP; g) and h) 5%PANI -MRP.

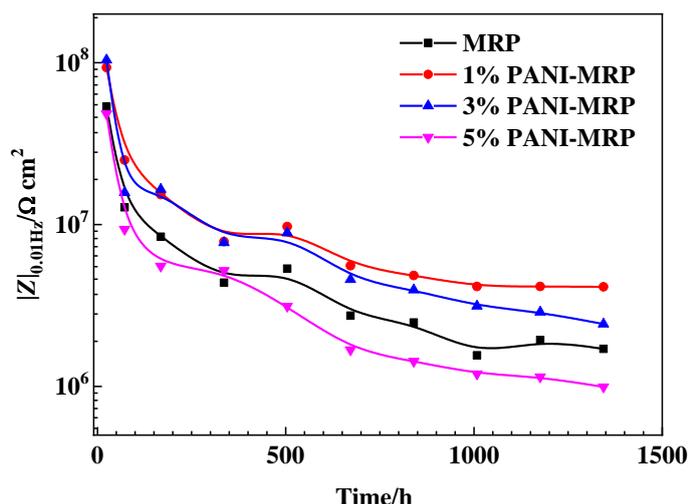


Figure 4. The variations of $|Z|$ values (0.01 Hz) with immersion time in 3 wt% NaCl solution.

The electrical equivalent circuit (EEC) in Fig. 5 was employed to fit the EIS results. To obtain more precise results, the capacitive responses were fitted by constant phase elements, Q , whose impedance is defined as

$$Z_Q = \frac{1}{Y_0(j2\pi f)^n} \quad (1)$$

in which Y_0 is the CPE constant, $j = \sqrt{-1}$, f is the frequency (Hz), the exponent n is equal to $\alpha/(\pi/2)$, and α the phase angle of the CPE (radians).

The EEC in Fig. 5 was employed in the previous studies of MRP on AZ91D substrates [17-19, 21]. Where, Q_c and R_c are coating capacitance and coating resistance, respectively. Q_{dl} is the double layer capacitance at the Mg particles/electrolyte interface and R_{ct} is the charge-transfer resistance of the Mg particles. The capacitance Q_{diff} in parallel to resistance R_{diff} can be noted as Z_{diff} , which could be correlated to diffusion processes caused by the presence of corrosion products of Mg particles [17-23].

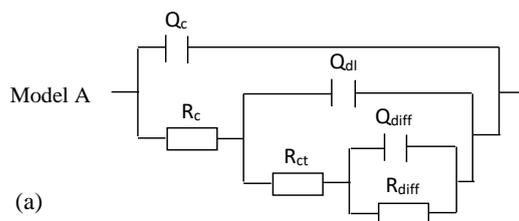


Figure 5. Equivalent electrical circuits used to fit EIS results: a) stable stage, b) late stage.

The changes of coating resistance R_c and charge-transfer resistance R_{ct} for different coatings are shown in Fig. 6. R_c is often used to characterize the number of pores or capillary channels through which

the electrolyte penetrates into coatings [17]. In general, R_c decreases with prolonging immersion time due to the electrolyte permeation. It could be observed from Fig. 6 that the R_c values for all the coatings decreased sharply in the initial immersion time and then showed an increase. This phenomenon might be explained by the initial electrolyte permeation and the subsequent precipitation of corrosion products in coatings. Although the R_c values of MRP was higher than the other coatings in the initial and medium immersion, it decreased suddenly after 144 hours of immersion while the R_c values of the other coatings declined gradually. For the 1% and 3% PANI containing coatings, the R_c values began to decrease gradually and were higher than that of MRP after 504 hours of immersion, indicating that the addition of PANI particles could enhance the coating stability.

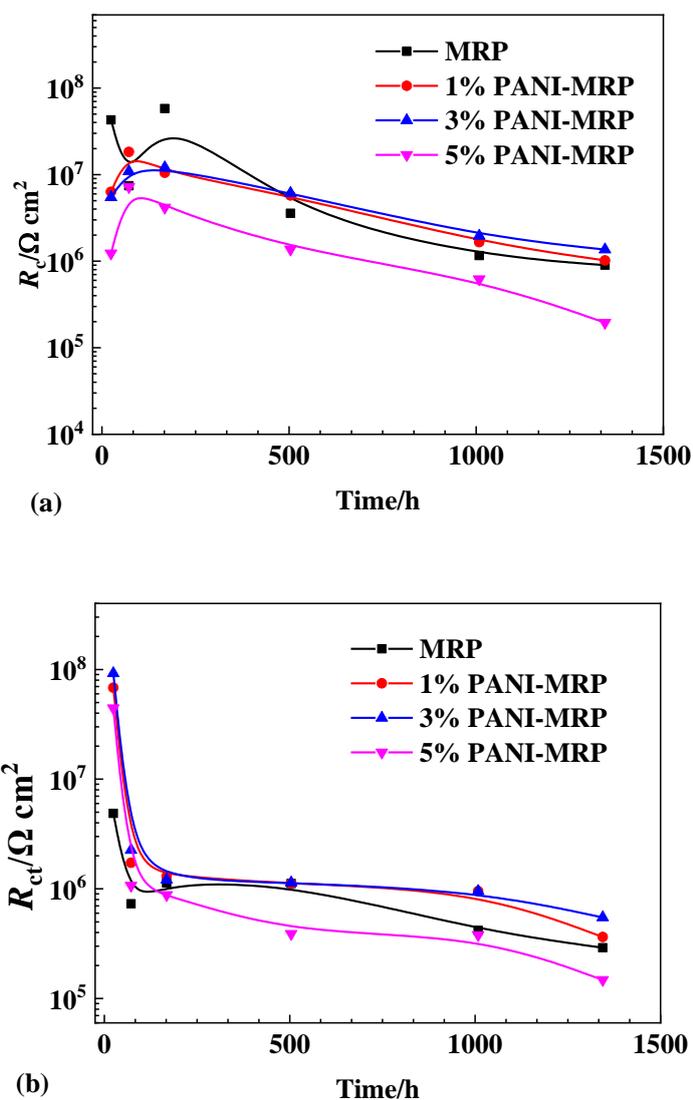


Figure 6. The changes of the obtained impedance parameters with time: (a) coating resistance, R_c ; (b) charge-transfer resistance R_{ct} .

R_{ct} is utilized to characterize the electrochemical reaction activity of Mg particles in the coatings and the interface stability between Mg particles and binder [17, 23]. Initially a thin layer of Mg oxide enveloped the Mg particle. As electrolyte permeated into the coatings, the oxide film was dissolved and

more Mg particles exposed, leading to the decline of R_{ct} values. Subsequently, the R_{ct} values of MRP coated sample showed an increase due to the accumulation of Mg corrosion products. As the immersion time prolonged, MRP deteriorated gradually and the micro defects in the coatings. The R_{ct} values of 1%PANI- MRP and 3%PANI-HF/MRP were higher than those of MRP after 504 hours of immersion. It could be concluded from the changes of the R_{ct} that the PANI particles addition could reduce the electrochemical reaction activity of Mg particles and enhance the coating stability.

3.5 Substrate analysis

In order to study the effects of the PANI particles in MRP on 5083 alloy, SEM were applied to analyze the substrate underneath the MRP and the 1% PANI-MRP after EIS measurements in 3 wt% NaCl slution. The SEM images of the substrates underneath different coatings after immersion in 3 wt% NaCl solution were displayed in Fig. 7. By comparing the alloy substrate underneath the different coatings, it could be found that a large area of white oxide film covered the underlying substrate of MRP. Moreover, only a few white oxide films appeared on the substrate surface underneath the 1% PANI-MRP, demonstrating that the addition of the PANI particles could retard the corrosion of the 5083 substrate. Therefore, it could be inferred that the reaction activities of the Mg particles in coatings could be impeded by the PANI particles to reduce their consumption rate.

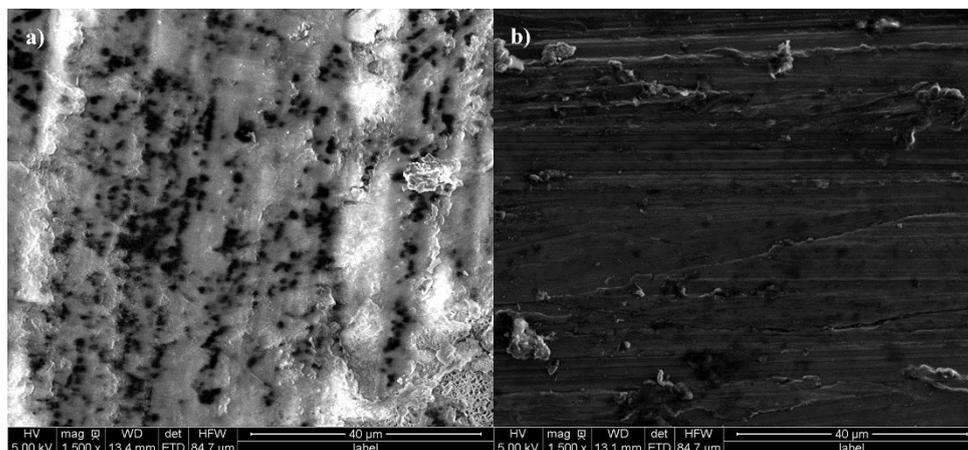


Figure 7. SEM images of the substrate surface underneath different coatings after 1344 hours of immersion: (a) MRP; (b) 1 % PANI- MRP.

The protective mechanism of MRP containing PANI particles for 5083 alloy is similar to that of MRP with HF doped PANI particles on AZ91D alloy. In the initial stage, the PANI particles with a proper content improved the electrical contact of Mg particles and 5083 substrate, leading to the enhancement of the cathodic protection (Fig. 2). Next, the PANI particles could improve the compactness of the products of Mg particles, improving barrier effects of the coating (Fig. 3, 4 and 6). Meanwhile, the PANI particles could retard the reaction activities of the Mg particles in coatings, thereby reducing their consumption rate (Fig. 6 and 7).

4. CONCLUSIONS

(1) PANI was added in a MRP to improve the coating protective performance on 5083 alloy. The PANI particles enhanced the protective properties of the MRP on 5083 alloy obviously and the MRP loaded with 1 wt% PANI particles showed the best protective performance.

(2) Open circuit potential results showed that the 1 wt% PANI particles loading led to an enhancement of the cathodic protection in MRP and strengthened the coating barrier effect. EIS results showed that the PANI particles addition could reduce the electrochemical reaction activity of Mg particles and enhance the coating stability.

(3) The protective mechanism of MRP containing PANI particles for 5083 alloys is illustrated as follows. Firstly, the PANI particles with a proper content improved the electrical contact of Mg particles and 5083 substrate, leading to the enhancement of the cathodic protection. Secondly, the PANI particles could improve the compactness of the products of Mg particles, improving barrier effects of the coating. Finally, the PANI particles could retard the reaction activities of the Mg particles in coatings, thereby reducing their consumption rate.

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References

1. O.F. Hosseinabadi, M.R. Khedmati, *Ocean Eng.*, 232 (2021) 109153.
2. F. Deflorian, S. Rossi, M. Fedel, *Corros. Eng. Sci. Techn.*, 46 (2011) 237.
3. E. Canepa, R. Stifanese, L. Merotto, P. Traverso, *Mar. Struct.*, 59 (2018) 271.
4. A.A. Olajire, *J. Mol. Liq.*, 269 (2018) 572.
5. R. Zhao, P. Rupper, S. Gaan, *Coatings*, 7 (2017) 1.
6. S.G.R. Emd, S. Morsch, T. Hashimoto, Y. Liu, S.R. Gibbon, S.B. Lyon, X. Zhou, *Prog. Org. Coat.*, 137 (2019) 105340.
7. M.E. Nanna, G. P. Bierwagen, *JCT Res.*, 1 (2004) 69.
8. D. Battocchi, A. M. Simões, D. E. Tallman, *Corros. Sci.*, 48 (2006) 1292.
9. D. Battocchi, A.M. Simões, D.E. Tallman, G.P. Bierwagen, *Corros. Sci.*, 48 (2006) 2226.
10. A.M. Simões, D.E. Tallman, G.P. Bierwagen, *Corros. Sci.*, 49 (2007) 3838.
11. A.M. Simões, D. Battocchi, D. Tallman, G. Bierwagen, *Prog. Org. Coat.*, 63 (2008): 260.
12. G. Bierwagen, D. Battocchi, A. Simes, A. Stammes, D. Tallman, *Prog. Org. Coat.*, 59 (2007) 172.
13. M. Yan, V.J. Gelling, B.R. Hinderliter, D. Battocchi, D.E. Tallman, *Corros. Sci.*, 52 (2010) 2636.
14. S. S. Pathak, M. D. Blanton, S. K. Mendon, J. W. Rawlins, *Corros. Sci.*, 52 (2010) 1453.
15. B.J.E. Merten, D. Battocchi, G.P. Bierwagen, *Prog. Org. Coat.*, 78 (2015) 446.
16. J. Lin, C. Orgon, D. Battocchi, G.P. Bierwagen, *Prog. Org. Coat.*, 102 (2017) 138.
17. X. Lu, Y. Zuo, X. Zhao, Y. Tang, X. Feng, *Corros. Sci.*, 53 (2011) 153.

18. X. Lu, Y. Zuo, X. Zhao, Y. Tang, *Electrochim. Acta*, 93 (2013) 53.
19. X. Lu, Y. Zuo, X. Zhao, S. Shen, *Int. J. Electrochem. Sci.*, 10 (2015) 9586.
20. P. Xu, X. Lu, H. Cheng, X. Feng, Z. Zhao, Y. Ding, Y. Shen, X. Shi, *Prog. Org. Coat.*, 135 (2019) 591.
21. X. Lu, S. Sun, Q. Fan, X. Pei, Y. Dun, X. Feng, C. Zou, W. Lu, *Coatings*, 9 (2019) 649.
22. X. Feng, C. Zhu, X. Lu, Y. Zhang, T. Wu, Y. Zuo, X. Zhao, Y. Dun, M. Wang, *Prog. Org. Coat.*, 141 (2020) 105550.
23. X. Lu, X. Wang, S. Chen, J. Cai, H. Tao, Z. Xu, X. Feng, *Int. J. Electrochem. Sci.*, 16 (2021) 211239.
24. S. Sathiyarayanan, S.S. Azim, G. Venkatachari, *J. Appl. Polym. Sci.*, 107 (2008) 2224.
25. G. Williams, H.N. McMurray, *Electrochim. Acta*, 54 (2009) 4245.
26. M.G. Hosseini, M. Jafari, R. Najjar, *Surf. Coat. Tech.*, 206 (2011) 280.
27. G. Gupta, N. Birbilis, A.B. Cook, A.S. Khanna, *Corros. Sci.*, 67(2013) 256.
28. N. P. Tavandashti, M. Ghorbani, A. Shojaei, J.M.C. Mol, H. Terryn, Y. Gonzalez-Garcia, *Corros. Sci.*, 112 (2016) 138.

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