

Corrosion Properties of the Polypyrrole-molybdate Film Electro-polymerized on the AZ31 Mg Alloy

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Abstract: The polypyrrole (PPy) coating and polypyrrole-molybdate (PPy-MoO₄²⁻) coating were electro-polymerized in sodium salicylate solution by cyclic voltammetry (CV) on the AZ31 Mg alloy surface. Surface morphology of PPy coating and PPy-MoO₄²⁻ coating on Mg alloy surface before and after being corrupted was observed by scanning electron microscopy (SEM). Attenuated total reflection-infrared (ATR-IR) spectra showed the characteristic ring stretching peaks of the PPy coating and PPy-MoO₄²⁻ coating, and also revealed the influence of MoO₄²⁻ on the characteristic ring stretching peaks on PPy. The surface resistance was measured by four-point probe method. The open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization analyzed the corrosion resistance performance of PPy coating and PPy-MoO₄²⁻ coating on the Mg alloy surface in 3.5% NaCl solution immersing for 12 h. The results show that the surface morphology of PPy-MoO₄²⁻ coating is compact. And the corrosion current density of PPy-MoO₄²⁻ coating is lower three orders than that of the PPy coating. The PPy-MoO₄²⁻ coating on the Mg alloy surface has better corrosion resistance and smaller surface resistance than the PPy coating because of the existence of the molybdate ion.

Key words: polypyrrole-molybdate; cyclic voltammetry; magnesium alloy; corrosion

Magnesium is one of the most abundant metals on the earth and is the lightest in the practical metals^[1]. Mg alloys play essential roles in vessels, aerospace, automotive, 3C and other fields, because of the outstanding performances: high specific strength, large elastic modulus and coefficient of thermal conductivity, good shock resistance and impact resistance, excellent machining performance and good organic and alkali corrosion resistance performance^[2]. However, Mg alloys are easy to be corroded due to the low potential (-2.73 V)^[3]. The corrosion resistance hinders its application, while appropriate treatment on the surface of Mg alloys can improve the corrosion resistance.

Chemical conversion coatings^[4], metal coatings^[5], anodic oxidation films^[6], ion implantation^[7], vapor deposition^[8] and organic membranes^[9] are the common surface treatment technology. The organic membranes are more common^[10]. Recently, conductive polymers become a hot topic, as traditional organic membranes reduce the conductivity of the

materials and application of Mg alloys in electronic communications and aerospace is increased^[11]. Thus conductive polymer films meet the requirements of corrosion resistance, electromagnetic shielding and good adherence, which can well make Mg alloys be used in electronic communications and aerospace.

Polypyrrole (PPy), the typical conductive polymer has many advantages, such as convenient synthesis, good oxidation resistance, high conductivity, easy to film, soft, non-toxic^[12]. PPy has always been used in biology, super capacitor, anti-static materials, electromagnetic shielding materials, metal anticorrosion, etc. PPy film protects Mg alloys from corrosion by playing the roles of passivation and shielding^[13], which can increase self corrosion potential and reduce corrosion rate of Mg alloys. Chemical oxidation^[14] and electric polymerization^[15] are the methods to synthesize PPy, in which chemical oxidation is suitable for the preparation of solid powdered polypyrrole while the

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processing is difficult and the mechanical performance is poor. While the electric polymerization method adopts the three-electrode system under the control of electric field^[16]. The monomer pyrrole (Py) is polymerized to form the polypyrrole film on the surface of Mg alloys. The method to polymerize polypyrrole is applied in the treatment of Cu^[17] and steel^[18] maturely, but fewer are used on the surface of active metals such as magnesium alloys.

Turhan^[19] used cyclic voltammetry eletro-polymerized PPy film on AZ91D magnesium alloy surface in salicylate solution. The results showed that it had improved the corrosion resistance of Mg alloys. A. Srinivasan^[3] studied the properties of polypyrrole film on the AZ31 magnesium alloys. By characterization methods of ATR-IR, SEM, AFM and EIS, it revealed the films were rough and were similar to cauliflowers, and corrosion resistance had been improved. The yellow-black film was synthesized on AZ91 Mg alloys by Y. F. Jiang et al.^[20] This electric polymerization reaction occurred in alkaline solution. And different morphology had been formed by different pretreatment which affected potentiodynamic curves.

V. Karpakam^[21] reported the electro-synthesis of PANI-MoO₄²⁻ film on steel. The effect of MoO₄²⁻ seemed to passivator and passive layer was formed before the electro-polymerization reaction occurred. In this paper, the electrolyte was sodium salicylate which included pyrrole and MoO₄²⁻. The PPy-MoO₄²⁻ coating was carried out by cyclic voltammetry on AZ31 Mg alloys surface. The surface morphological was analyzed by scanning electron microscopy (SEM) and attenuated total reflection-infrared (ATR-IR) spectra. The corrosion resistance of PPy film and PPy-MoO₄²⁻ was also discussed applying open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization.

1 Experiment

The composition and mass ratio of AZ31 Mg alloys have been shown in Table 1. All the samples (17 mm×17 mm×1 mm) made of AZ31 Mg alloys were ground with 320 #, 800 # and 1000 # SiC grit emery paper and cleaned in 1:1 (vol%) ethanol: acetone mixture for 10 min in ultrasonic bath. Then the samples were washed with distilled water. The electrolyte is a solution containing sodium salicylate. All cleaned samples were divided into two groups. One of them had been put into an electrolyte solution of 0.5 mol L⁻¹ sodium salicylate + 0.05 mol L⁻¹ pyrrole (Py), while the electrolyte solution of the other group contained 0.5 mol L⁻¹ sodium salicylate + 0.05 mol L⁻¹ Py + 0.01 mol L⁻¹ MoO₄²⁻. The electro-polymerization reactions of the two groups were achieved in the recumbent electrolytic cell with three-electrode system in which AZ31 Mg alloy was used as working electrode, Hg/HgCl₂ was regarded as reference electrode and Pt wire was treated as counter electrode by cyclic voltammetry

Table 1 Composition and mass ratio of AZ31 Mg alloy (wt%)

Element	Al	Zn	Mn	Cu	Mg
Content	2.83	0.8	0.37	0.002	Bal.

(CV) between 0.6 V and 2.0 V of sweeping potential at a scan rate of 7 mV/s for 10 cycles.

Scanning electron microscopy micrographs were obtained using JSM-6480A. Attenuated total reflection-infrared (ATR-IR) spectral analysis of the electrodeposited films on AZ31 Mg alloys was performed with a Perkin Elmer- Spectrum-two spec trophotometer. Surface resistance was measured by a four-point probe method.

The corrosion resistance performance of the uncoated and PPy and PPy-MoO₄²⁻ coated alloys were evaluated through three methods with electrochemical workstation: open circuit potential, electrochemical impedance spectroscopy and potentiodynamic polarization. EIS over the frequency range from 10 kHz to 0.1 Hz with 20 mV amplitude, potentiodynamic polarization at the scan rate of 1 mV/s and open circuit potential varying with time were measured in 3.5% NaCl for 12 h immersion using the above mentioned three-electrode system in which AZ31 Mg alloy and coated alloys were used as working electrode (WE), Hg/HgCl₂ was regarded as reference electrode (RE) and Pt wire was treated as counter electrode (CE).

2 Results and Discussion

2.1 Electrochemical polymerization

The electrochemical polymerization of pyrrole (Py) and Py-MoO₄²⁻ is finished by cyclic voltammetry between 0 and 2.0 V of scan potential at 7 mV/s for 10 cycles in the solution of 0.5 mol L⁻¹ sodium salicylate + 0.05 mol L⁻¹ Py and 0.5 mol L⁻¹ sodium salicylate + 0.05 mol L⁻¹ Py + 0.01 mol L⁻¹ MoO₄²⁻, respectively. The first cycle and CV of polymerized PPy and PPy-MoO₄²⁻ are shown in Fig.1.

No matter it is PPy or PPy-MoO₄²⁻ coating on the Mg alloys, there is a peak between 0 and 0.5 V at the anodic sweep, which indicates the dissolving of the A31 Mg alloy^[3]. The Fig.1a shows the first cycle electro-synthesized PPy and PPy-MoO₄²⁻ on the Mg alloy surface. The first anodic peak current of the PPy coating is lower than the PPy-MoO₄²⁻ coating during the first cycle CV, and hence the dissolution of Mg alloy of PPy-MoO₄²⁻ coating is larger than that of the PPy coating. Because the sodium salicylate solution contains MoO₄²⁻, both the sodium salicylate and MoO₄²⁻ can form a passivation film on the Mg alloy surface. Fig.1b reveals the CV of electro-polymerized PPy on the Mg alloy surface. The first anodic peak at about 0.2 V means the dissolution of Mg alloy and the second anodic peak at about 0.9 V indicates the oxidation of Py which polymerizes to form PPy film. At the beginning cycles of the CV, the second peak at about 0.9 V is attributed to the

oxidation of salicylate. Then the peak currents of subsequent cycles increase with increasing number of cycles, which indicates the formation of PPy. Under the electric field, Py monomer is activated to become the radical cation which is unstable and polymerizes with another radical cation to form dimer or trimer, and it gradually grows into PPy. A slight current increment at the end of each cycle confirms the polymer film growth. As can be seen in Fig.1c peaks at about 0.2 and 1.1 V appear which correspond to the dissolution of the Mg alloy and oxidation of Py. Comparing the CV of PPy and PPy-MoO₄²⁻ formation on the AZ31 Mg alloys surface, the oxidation potential of Py rises to 1.1 V. The different oxidation potential of the two conditions probably is attributed to MoO₄²⁻ in the sodium salicylate solution, which makes the oxidation potential of Py shift to positive due to the inhibitive nature of MoO₄²⁻ [21].

2.2 Surface morphological analysis

Fig.2 reveals the surface morphology of the substrate, PPy coating and PPy-MoO₄²⁻ coating on the AZ31 Mg alloy surface using scanning electron microscopic in different

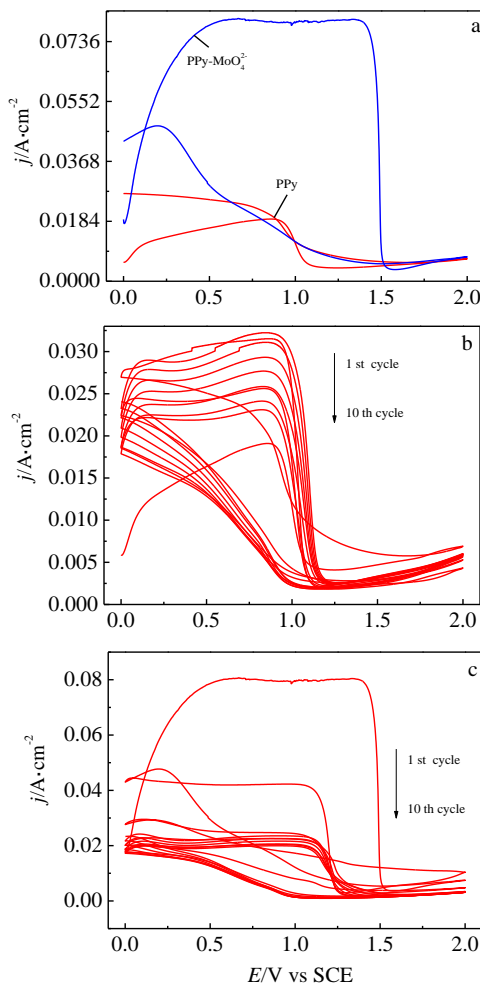


Fig.1 First cycle electro-synthesized PPy and PPy-MoO₄²⁻ (a), CV of electro-synthesized PPy (b), and CV of electro-synthesized PPy-MoO₄²⁻ (c) on AZ31 Mg alloys

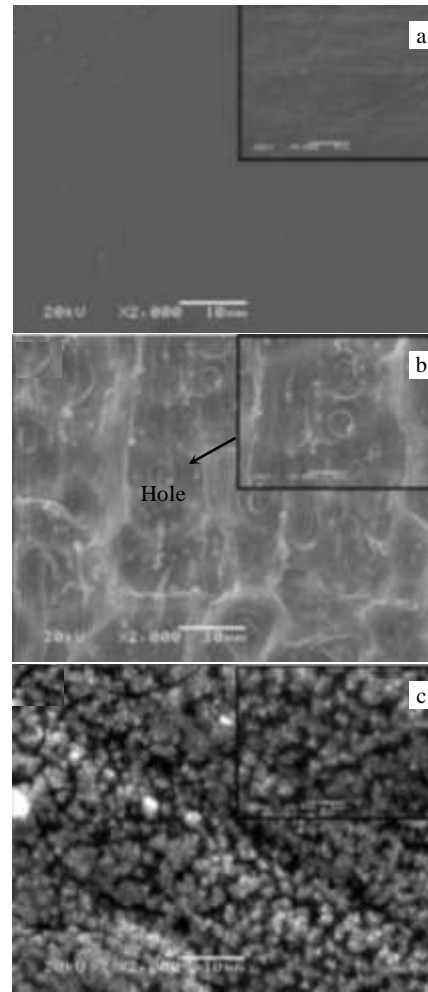


Fig. 2 SEM microstructures of bare AZ31 Mg alloy (a), PPy coating (b), and PPy-MoO₄²⁻ coating (c)

multiple scanning. Fig.2a which shows the surface morphologies of the Mg alloy substrate indicates that alloy surface is smooth. The surface morphology of PPy coating and PPy-MoO₄²⁻ coating on the alloy surface is shown in Fig.2b and Fig.2c, respectively. A marked difference is observed to contrast the Fig.2b and Fig.2c. The microstructure of PPy coating is porous, which increases probability that corrosive media enter the interior to corrode the alloy. However, this disadvantage doesn't exist in the PPy-MoO₄²⁻ coating in Fig.2c. The surface morphology of the PPy-MoO₄²⁻ coating is different from that of PPy coating. There are many like lump accumulations to achieve sealing effect, which can protect the alloy from corroding. The special microstructure may be formed due to interaction of MoO₄²⁻ and polymer chains. The section scanning electron microscopy of the PPy coating and PPy-MoO₄²⁻ coating on AZ31 Mg alloy is demonstrated in Fig.3. The thickness of coatings is almost the same. Therefore, the MoO₄²⁻ has little influence on the growth of coatings.

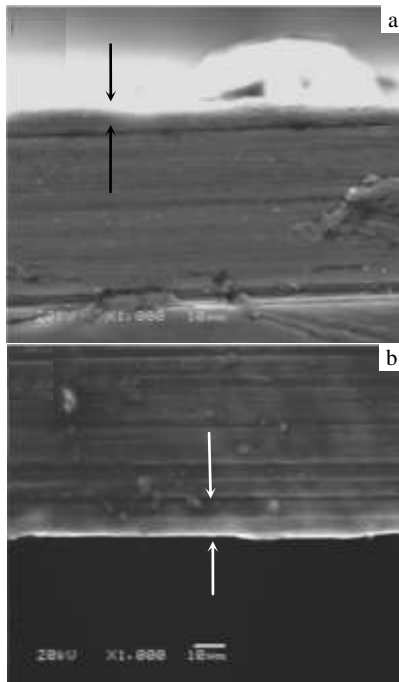


Fig.3 Section SEM images of PPY coating (a) and PPY-MoO₄²⁻ coating (b)

2.3 ATR-IR studies

The PPY film and PPY-MoO₄²⁻ film formed on AZ31 Mg alloy surface by CV were analyzed using ATR-IR spectroscopic studies and the ATR-IR spectroscopy are shown in Fig.4 and Fig.5. The peak appears at about 1580 cm⁻¹ which is attributed to the absorption peak of the C=C stretching vibration. The peak around 1250 cm⁻¹ is due to the stretching vibration of C-N. The characteristic peaks of PPY are detected around 1455, 1384, 1040, 930 and 755 cm⁻¹. The peaks at 699.19 and 701.96 cm⁻¹ for PPY-MoO₄²⁻ coating correspond to the stretching vibrations and bending of molybdate^[21]. The surface resistance of PPY film is 4.3 mΩ, while the surface resistance of PPY-MoO₄²⁻ has decreased to 3.6 mΩ.

2.4 Corrosion studies

2.4.1 Electrochemical test

The open circuit potential of PPY coating, PPY-MoO₄²⁻ coating and the uncoated Mg alloy were investigated periodically by immersing in 3.5% NaCl for 12 h. And the curves of open circuit potential (OCP) varying with time are shown in Fig.6. At first, the potential of the bare Mg alloy is about -1.48 V, then the potential is stable after 2 h, while the stable potentials of the PPY coating and PPY-MoO₄²⁻ coating are at about after 1 h. It may be due to the quicker formation of corrosion product layer on the coated Mg alloys than that of the bare Mg alloy, which can be earlier to protect the Mg alloy from corrosion. The stable potential of PPY coating and PPY-MoO₄²⁻ coating is about -1.461 and -1.451 V, respectively, which indicates the

PPY-MoO₄²⁻ coating can resist the corrosive ion penetration through the film to the metal surface. Hence the MoO₄²⁻ can provide double protection for the Mg alloy.

The electrochemical impedance of bare AZ31 Mg alloy and PPY and PPY-MoO₄²⁻ coating obtained at the OCP after 12 h of immersion in 3.5% NaCl solution are compared in Fig.7. The Nyquist shapes of uncoated, PPY coating and PPY-MoO₄²⁻ coating are similar, which consist of the capacitive reactance and inductive reactance. The capacitive reactance appear in the high frequency region manifests the control by the charge mass transfer process. The

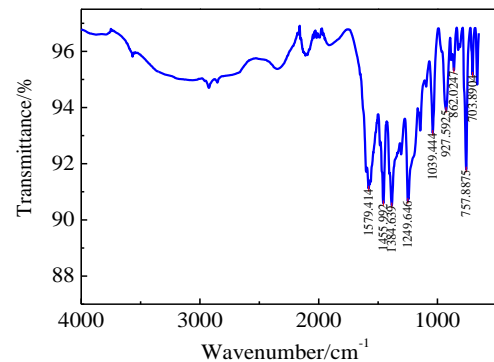


Fig.4 ATR-IR spectrum for PPY coating

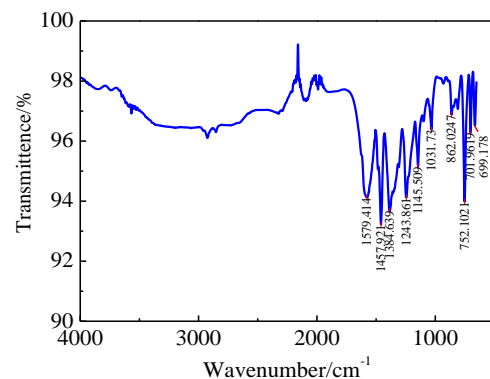


Fig.5 ATR-IR spectrum for PPY-MoO₄²⁻ coating

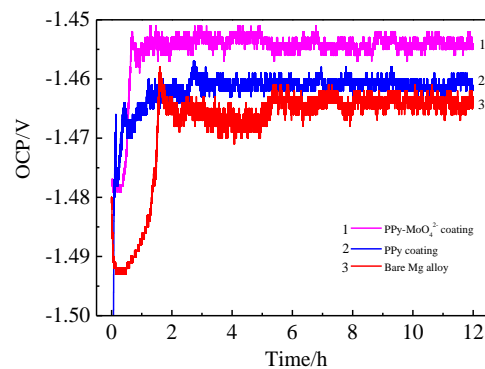


Fig.6 OCP-time curves of PPY-MoO₄²⁻ coating, PPY coating and bare Mg alloy

higher the capacitive reactance arc radius is, the bigger the impedance value of coating is, so that it is difficult that the corrosion media enter to corrode the substrate. The impedance value of PPy-MoO₄²⁻ coating (210 Ω cm²) is bigger than that of the PPy coating (187 Ω cm²) whose impedance is bigger than that of the bare Mg alloy (137 Ω cm²), hence the coating on the Mg alloy surface can improve the corrosion resistance performance, and the PPy-MoO₄²⁻ coating on the AZ31 Mg alloy surface has the better corrosion resistance than PPy coating. The inductive reactance arc diameter of PPy-MoO₄²⁻ coating in the low frequency is slightly larger than others, which may be attributed to the decrease in the adsorbed corrosive ions from the NaCl solution.

Potentiodynamic polarization curves of the PPy coating, PPy-MoO₄²⁻ coating and the bare Mg alloy after 12 h of immersion in 3.5% NaCl solution are shown in Fig.8. In the polarization curves, it is clearly observed that the corrosion current density (j_{corr}) of the PPy-MoO₄²⁻ coating (9.896×10^{-9} A cm⁻²) is lower than that of the PPy coating (9.266×10^{-6} A cm⁻²) and the substrate (1.011×10^{-5} A cm⁻²). While the i_{corr} of the PPy coating is close to that of the bare Mg alloy. These results indicate that the PPy-MoO₄²⁻ coating on the Mg alloy surface can offer enhanced corrosion resistance compared with the only PPy coating on the Mg alloy surface. The lower j_{corr} of the PPy-MoO₄²⁻ coating may be attributed to the existence of MoO₄²⁻ that offers better corrosion protection due to the formation of passive film along with the formation of MoO₄²⁻ complex film.

2.4.2 Surface morphological analysis after corrosion

The surface morphological analysis after corrosion in 3.5% NaCl for 12 h of PPy coating and PPy-MoO₄²⁻ coating on Mg alloy is shown in Fig.9. The corrosion pattern of the PPy coating and PPy-MoO₄²⁻ coating belongs to the total corrosion, which has a little danger coefficient compared with local corrosion. Corrosion of PPy-MoO₄²⁻ coating is uniform. However, there are many fractures when PPy

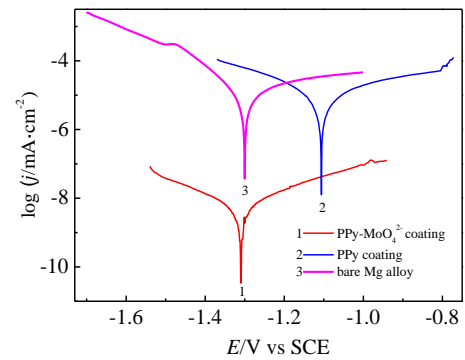


Fig. 8 Potentiodynamic polarization curves of PPy-MoO₄²⁻ coating, PPy coating and bare Mg alloy

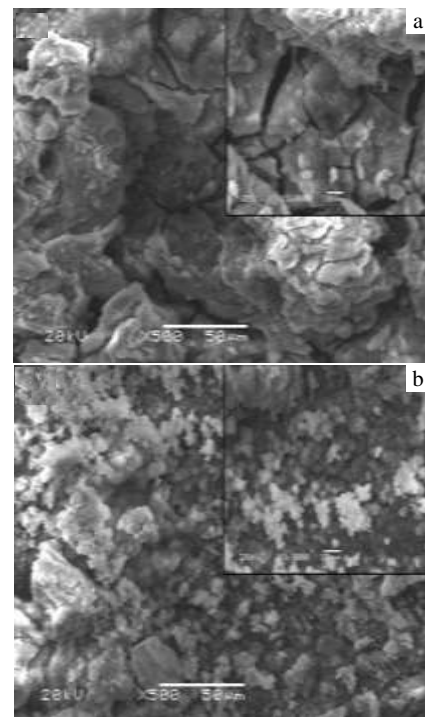


Fig. 9 SEM morphologies of PPy coating (a) and PPy-MoO₄²⁻ coating (b) after corrosion

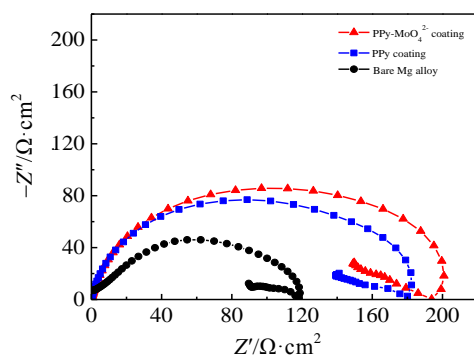


Fig. 7 Nyquist plots of PPy-MoO₄²⁻ coating, PPy coating and bare Mg alloy

coating on the Mg alloy is corroded. And the microstructure of the PPy coating is looser than that of the PPy-MoO₄²⁻ coating. Moreover, the corrosion pit of the PPy-MoO₄²⁻ coating is regular.

3 Conclusions

1) The surface resistance of PPy-MoO₄²⁻ coating is smaller than that of the PPy, which can be applied in aerospace field. The electro-polymerized PPy coating on the AZ31 Mg alloy surface can offer the protection Mg alloy from corrosion, but the corrosion resistance performance is

not better than the PPy-MoO₄²⁻ coating.

2) MoO₄²⁻ can form the MoO₄²⁻ complex passive film on the Mg alloy surface before the Py polymerizes. Synergy between PPy and MoO₄²⁻ makes the film surface morphology become compact, and prevents the iron-corrosion penetration to the Mg alloy surface, which can improve the corrosion resistance performance.

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AZ31 镁合金表面聚吡咯-钼酸盐膜的腐蚀性能

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摘要: 在水杨酸钠溶液中采用循环伏安法在AZ31镁合金表面分别电聚合聚吡咯(PPy)膜和聚吡咯-钼酸根膜(PPy-MoO₄²⁻)。利用扫描电子显微镜(SEM)观测PPy膜和PPy-MoO₄²⁻膜层腐蚀前后的表面形貌, 衰减全反射红外光谱(ATR-IR)反映了PPy膜和PPy-MoO₄²⁻膜的特征吸收峰, 研究了MoO₄²⁻的存在对PPy特征吸收峰的影响。使用四探针法测量薄膜的表面电阻; 采用开路电位(OCP), 电化学交流阻抗谱(EIS)和动电位极化曲线测试PPy膜和PPy-MoO₄²⁻膜在3.5%NaCl溶液中浸泡12 h后的耐腐蚀性能。结果显示, PPy-MoO₄²⁻膜层更紧凑, PPy-MoO₄²⁻膜层的腐蚀电流密度比 PPy 膜的低 3 个数量级。钼酸根的存在使得PPy-MoO₄²⁻膜的表面电阻比PPy膜小, 且PPy-MoO₄²⁻膜的耐腐蚀性能较好。

关键词: 聚吡咯-钼酸盐; 循环伏安; 镁合金; 腐蚀性

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