Enhancing the anti-corrosion performance of ZIF-8-based coatings via microstructural optimization†

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Although still in their infancy, MOF-based coatings have shown great potential for their applications as anti-corrosion coatings. Nevertheless, an in-depth investigation of the influence of morphology on their anti-corrosion performance has rarely been conducted. In this study, ZIF-8-based anti-corrosion coatings with diverse microstructures were prepared by the facile hydrothermal growth of ZnAl–NO3 LDH buffer layers followed by solvothermal treatment with ZIF-8 precursor solutions with different recipes. DC polarization tests demonstrated that the precursor solution containing only 2-methylimidazole led to the formation of ZIF-8–ZnAl–NO3 LDH composite coatings with superior anti-corrosion performances probably due to the reduced grain boundary defect density.

Introduction

The corrosion of metals and their alloys will result in severe economic and safety issues. Chromate-containing conversion coatings, which have historically been considered as an effective anti-corrosion method for metallic substrates, have been restricted because of their toxic and carcinogenic properties.1–3 Therefore, new anti-corrosion materials with excellent anti-corrosion performance, easy processability, low manufacturing cost and improved sustainability are yet to be developed. Among various materials, layered double hydroxides (LDHs) provide a cost-effective and eco-friendly way to protect metals (like Al) against corrosion.4–7 For instance, laurate-intercalated ZnAl LDH films involving in situ hydrothermal growth and anion exchange with laurate have been prepared. The prepared LDH film exhibited low current density (≈ 10⁻⁹ A cm⁻²) in a DC polarization test.4 A recent study further indicated that the prepared ZnAl–NO3 LDH films not only acted as anti-corrosive coatings but were also involved in a self-healing process via the dissolution-recrystallization mechanism when exposed to a chloride-containing environment.5

Besides LDHs, diverse hydrophobic, water-stable and small pore-sized MOF materials (such as dopamine-grafted-MOF-5, [Zn₄C₆H₆]₉, ZIF-8,9 ZIF-90,12 Mg-MOF-74,13 Ag-MOFs,14 M(4-SO₃-pz)₂,15 LnPc216 and phosphate-based MOF17) have been prepared that exhibit unprecedented opportunities for anti-corrosion applications. For example, we recently synthesized well-intergrown ZIF-8 coatings on Al plates with excellent anti-corrosion performances by facile solvothermal growth.11 Nevertheless, to date, the effect of the microstructures of most MOF-based coatings on their anti-corrosion performance has not been well elucidated.

To further improve their anti-corrosion performance, MOF coatings should be well-intergrown, continuous, and firmly attached to the metal surface. In addition, the fabrication process should be simple, cost-effective and eco-friendly. Herein, we developed a facile approach to prepare ZIF-8-based anti-corrosion coatings with different microstructures by the simple solvothermal conversion of ZnAl–NO3 LDH buffer layers with different recipes. Under hydrothermal conditions, the surface of Al plates was partially reduced and Al³⁺ was released to the precursor solution; simultaneously, NO₃⁻ charge compensating anions were spontaneously intercalated into the interlayer galleries of ZnAl brucite-like sheets.18–20 Consequently, the ZnAl–NO3 LDH buffer layers were subjected to solvothermal treatment in a methanol solution containing 2-mIm (in some cases, additional Zn(NO₃)₂·6H₂O was added), which not only served as the organic linker of ZIF-8, but also promoted the dissolution of the ZnAl–NO3 LDH buffer layers via nucleophilic attack. Finally, the released Zn²⁺ coordinated with 2-mIm, leading to the formation of well-intergrown ZIF-8 coatings on Al plates. It should be noted that prolonging the reaction time resulted in a gradual decrease in the grain boundary defects in ZIF-8 coatings. After the formation of defect-free protective ZIF-8 surface coatings, further nucleophilic attack of 2-mIm underneath the ZnAl–NO₃ LDH buffer layers was effectively

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9nj05998a
at room temperature, the bare Al plate was vertically placed in a bath with vigorous stirring. After further stirring for 30 min, NH_4NO_3 (98.0 wt%, Shanghai Maklin Biochemical), Al plate was thoroughly cleaned by ultrasonic cleaning with deionized water. ZnAl–NO_3 LDH buffer layer with optimized microstructures was prepared by mixing 4.5 g Zn(NO_3)_2·6H_2O and 4.8 g NH_4NO_3 in 100 ml DI water. Consequently, 7 ml NH_3·H_2O (1 wt%) was slowly added into the precursor solution in an ice bath with vigorous stirring. After further stirring for 30 min at room temperature, the bare Al plate was vertically placed in a 50 ml Teflon-lined stainless vessel. After the hydrothermal reaction at 40 °C for 36 hours, the vessel was taken out and naturally cooled to room temperature in air.

Preparation of ZIF-8–ZnAl–NO_3 LDH coatings

The precursor solution was prepared by mixing 1.0 g of 2-mLM in 50 ml methanol. Then, the ZnAl–NO_3 LDH buffer layer-modified Al plate was vertically placed in a 50 ml Teflon-lined stainless vessel. After a solvothermal reaction at 80 °C for 36 hours, the vessel was taken out and cooled to room temperature in air.

Preparation of ZIF-8 coatings

The precursor solution was prepared by mixing 0.49 g of 2-mLM, 0.54 g of Zn(NO_3)_2·6H_2O and 0.27 g of sodium formate in 80 ml methanol. The ZnAl–NO_3 LDH buffer layer-modified Al plate was vertically placed in a 50 ml Teflon-lined stainless vessel. After the solvothermal reaction at 100 °C for 12 hours, the vessel was taken out and cooled to room temperature in air.

DC polarization test

A three-electrode system was carried out for DC polarization tests at room temperature on a CHI-660E electrochemical interface: a ZnAl–NO_3 LDH buffer layer-coated Al plate, a ZIF-8 layer-coated Al plate, a ZIF-8–ZnAl–NO_3 LDH layer-coated Al plate or a bare Al plate was used as the working electrode, a platinum electrode was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. A 3.5 wt% aqueous solution of NaCl was used as the corrosive medium. Before the test, the samples were immersed in the corrosive medium to measure the open-circuit-potential. The sweep rate and the potential range of the DC polarization test were 10 mV s⁻¹ and from −2.0 V to −0.4 V (vs. reference), respectively.

Results and discussion

Characterizations of MOF-based anti-corrosion coatings

The first step involved the fabrication of well-intergrown ZnAl–NO_3 LDH buffer layers. Herein, the influence of the reaction temperature and precursor solution composition on the final morphology of the ZnAl–NO_3 LDH precursor coatings was investigated. The optimal reaction conditions for preparing the LDH precursor layer could be determined by a series of experiments with precisely controlled variables. The SEM images indicate that the prepared ZnAl–NO_3 LDH buffer layers exhibit considerable uniformity and compactness under optimized reaction conditions; otherwise, substantial grain boundary defects, which may adversely affect the morphology and anti-corrosion performance of the ZIF-8 coatings, would appear (shown in Fig. 2).

As shown in Fig. 3a, after in situ hydrothermal growth, the surface of the Al plates was uniformly covered with closely-packed plate-like LDH crystals. Moreover, the LDH crystals were vertically aligned on the Al plates, as could be interpreted by the “selective evolution”, a principle proposed by Van der Drift in the interpretation of the preferred orientation of a vapor-deposited PbO layer. The cross-sectional image further
demonstrated that the ZnAl–NO₃ LDH buffer layers were uniform with a thickness of 2 μm (Fig. 3b). In addition, the XRD pattern confirmed that the formed coatings indeed belonged to the pure LDH phase with the 2θ value of 10.0°, corresponding to a basal spacing of 8.86 Å, which was characteristic of NO₃⁻/CO⁻ intercalated ZnAl–LDHs (Fig. 4a).²²,²³

In the next step, the ZnAl–NO₃ LDH buffer layers were further immersed in a methanol solution containing 2-mIm. Our results demonstrated that increasing the concentration of 2-mIm promoted the release rate of Zn²⁺ and the growth rate of the ZIF-8 coatings (shown in Fig. 5). After the solvothermal treatment of the ZnAl–NO₃ LDH buffer layers under optimized conditions, it was found that well-intergrown ZIF-8 coatings with a grain size of 0.5 μm (Fig. 6a) and a thickness of 2.4 μm (Fig. 6b) were formed. Simultaneously, the thickness of the parent ZnAl–NO₃ buffer layers were reduced to 0.45 μm (inset of Fig. 6b). No marginal gap between the ZnAl–NO₃ LDH buffer layers and the ZIF-8 coatings was observed, therefore indicating high-affinity interactions between the ZnAl–NO₃ LDH and ZIF-8 phases. The partial conversion of the ZnAl–NO₃ LDH buffer layers could be attributed to the rapid formation of defect-free protective ZIF-8 surface coatings, which effectively prevented further nucleophilic attack of 2-mIm on the remaining ZnAl–NO₃ LDH buffer layers, as confirmed by our previous research.²⁴ The formation of the ZIF-8–ZnAl–NO₃ LDH composite coatings was potentially advantageous for the concurrent enhancement in both anti-corrosion and scratch adhesion performances. In addition, the XRD pattern of the prepared coatings (Fig. 4b) indicated that the new emerging diffraction peaks matched well with the standard diffraction pattern of the pure ZIF-8 phase. Nevertheless, it was impossible to accurately identify the diffraction peaks derived from the LDH phase owing to severe peak overlapping between the ZIF-8 and ZnAl–NO₃ LDH phases.

Besides the above-mentioned experiment, a comparative experiment involving the solvothermal treatment of the ZnAl–NO₃ LDH buffer layers with a precursor solution containing both Zn(NO₃)₂·6H₂O and 2-mIm was also conducted. After the solvothermal treatment, it was found that well-intergrown ZIF-8 coatings with a grain size of 5 μm (Fig. 6c), which was significantly larger than that of the above-mentioned ZIF-8–ZnAl–NO₃ LDH composite coatings, were formed. This could be attributed to the much lower nucleation density of the ZIF-8 crystals on the Al plates. Indeed, owing to the slow release of Zn²⁺ from the ZnAl–NO₃ LDH buffer layers and the rapid dissolution of Zn(NO₃)₂·6H₂O in the bulk solution, nucleation of the crystal growth of ZIF-8 mainly occurred in the bulk.
solution rather than on the Al plate surface, leading to the formation of the ZIF-8 coatings with a larger grain size and possibly higher grain boundary defect density.25 Moreover, we noted that after solvothermal treatment, the ZnAl–NO₃ LDH buffer layers completely disappeared possibly due to the slow growth rate of the protective ZIF-8 surface coatings, which was incapable of preventing further nucleophilic attack of 2-mIm. In addition, it was noted that the thickness of the ZIF-8 coatings reached 4.2 μm (Fig. 6d), which was attributed to the sufficient supply of nutrients (in particular Zn²⁺) in the bulk solution.

Evaluation of the corrosion resistance of films

DC polarization represents an effective tool for the evaluation of the performance of anti-corrosion coatings.25–29 In addition to the ZIF-8 coating-modified Al plates, the anti-corrosion performances of both ZnAl–NO₃ LDH coating-modified and bare Al plates were tested for reference. The results indicated that I_corr for bare Al plates reached ~10⁻⁴ A cm⁻² (Fig. 7a). After coating Al plates with the ZnAl–NO₃ LDH coatings, I_corr was reduced by one order of magnitude: ~10⁻⁵ A cm⁻² (Fig. 7b). A further large decrease in I_corr to ~10⁻⁷ A cm⁻² was achieved in the case of the ZIF-8–ZnAl–NO₃ LDH composite coating-modified Al plates (Fig. 7d), which was superior to that of most MOF-based anti-corrosive coatings30–34 (a detailed comparison of anti-corrosion performance is summarized in SI-1, ESI†). As shown in Fig. 8, given the similar thickness, the ZIF-8-coated Al plates exhibited significantly weakened absorbances at 995 cm⁻¹ (C-Q C–N twisting), 1146 cm⁻¹ (C–N bending and C–N bending), 2924–2960 cm⁻¹ (C–H stretching of CH₃), and 3134 cm⁻¹ (C–H asymmetric stretching), indicating the increase in the grain boundary defect density.

The strong adhesion of anti-corrosion coatings to the metal surface is of vital importance for their practical applications.37 Herein, a scratch test was employed to evaluate the adhesion strength of the ZIF-8–ZnAl–NO₃ LDH composite coatings to the Al plates. It was observed that no peeling occurred after scratching the composite coatings with a depth of 40 μm (as shown in SI-2, ESI†), which unambiguously demonstrated their strong adhesion to the Al plates (Fig. 9a and b). In contrast, the pure ZIF-8 coatings were mechanically unstable and could be easily peeled off from the Al plates upon scratching, which was possibly due to the absence of the ZnAl–NO₃ LDH phase serving as
diversity of water-stable MOF materials, it is anticipated that for their use in harsh environments. Considering the structural boundary defects of the ZIF-8 coatings and the co-existence of the performance and mechanical stability due to the reduced grain site coatings on Al plates that exhibited superior anti-corrosion protecting metals and their alloys against corrosion.

MOF-based composite anti-corrosion coatings with optimized morphology and thermal stability (as shown in SI-3, ESI†) making them attractive as well as their excellent compatibility with a wide variety of anti-corrosion materials, it is anticipated that our study can provide new insights into the morphological optimization and performance enhancement of MOF-based anti-corrosion coatings for advancing their practical applications in the future.

Conclusions

In summary, relying on a facile partial solvothermal conversion method, we successfully prepared ZIF-8–ZnAl–NO₃ LDH composite coatings on Al plates that exhibited superior anti-corrosion performance and mechanical stability due to the reduced grain boundary defects of the ZIF-8 coatings and the co-existence of the ZnAl–NO₃ LDH anti-corrosion coatings. Taking into consideration both morphological and chemical diversity of water-stable MOFs as well as their excellent compatibility with a wide variety of anti-corrosion materials, it is anticipated that our study can provide new insights into the morphological optimization and performance enhancement of MOF-based anti-corrosion coatings for advancing their practical applications in the future.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors are grateful to the Thousand Youth Talents Program, National Natural Science Foundation of China (21176231) and the Technology Innovation Team of Dalian University of Technology (DUT2017TB01) for financial support.

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