Study of catecholate-functionalized zinc complex on carbon steel and its application to corrosion resistance

Xihong Che, Ronghui Yuan1, Licheng Tang, Yudong Xiong, Mengfan Wu and Maihao Zhu

Zhejiang Light Industrial Products Inspection and Research Institute, Hangzhou 310018, China

1Corresponding author’s e-mail: ystriker@163.com

Abstract. This work investigated the corrosion resistance of an acceptable composite coating obtained from catecholate-functionalized zinc complex (CFZ). The ion distribution states of catechol and Zn(II) at different pH values were calculated, and the anticorrosion of coatings on carbon steel by means of neutral salt spray test were specifically monitored. CFZ-steel was fabricated using 30 min electrodeposition of CFZ/Na2SO4 media at pH 9 on carbon steel. Lower corrosion degree of CFZ-steel in salt spray during oxidation process meant slight amount of corrosion attack on the steel surface. Also, the growth tendency of corrosion rate was gradually reduced, indicating a nonlinear relationship between corrosion rate and contact time. This indicated electrodeposition of CFZ was not only appropriate for the practical application of composite coatings to corrosion resistance but also a key step for extending the service life of carbon steel.

1. Introduction
Electrodeposition of functional zinc composite has developed from general protections to functional decorations, and is one of the well-practiced plating systems [1,2]. Electrodeposited zinc-steel is influenced by the electrochemical parameters including current density, electrolyte concentration and deposition time [3]. The galvanized coating is a typical coating on the iron and steel substrates, which has a protection effect on the base metal [4]. Catechol has strong coordination capability, and its intramolecular hydroxyl groups can provide ligand atoms. Catechol complexes interact with metal ions through bonds [5-7], and are utilized in the derivative complexes with manganese and copper [8,9].

In the field of high-performance coating, zinc has attracted attention due to its unique chemical properties for corrosion resistance [10,11]. The mechanical strength of zinc is brittle whose crystal structure is hexagonal close-packed lattice [12]. The transition metal zinc shows good bridged coordination [13,14]. Based on the above-mentioned background, an acceptable composite coating was reported in this paper, particularly for electrodeposition of catecholate-functionalized zinc complex (CFZ) on carbon steel. The morphology of CFZ and deposited CFZ-carbon steel (CFZ-steel) were characterized with transmission electron microscopy (TEM) and scanning electron microscopy (SEM), respectively. The specific surface area of CFZ was analyzed by Brunauer-Emmett-Teller (BET) method. Additionally, the distribution fraction of CFZ and the corrosion resistance of CFZ-steel were investigated.
2. Experimental section

2.1. Instruments and chemicals
The instruments included a Talos F200S transmission electron microscope (USA), a Nova NanoSEM 630 scanning electron microscope (USA), a Micromeritics ASAP2010 specific surface analyzer (USA), a CM HY-60 salt spraying machine (China), a CorrTest CS350H electrochemical workstation (China) and a Leici PHSJ-5 pH meter (China).

20# carbon steel was purchased from Aida Technology (China). Catechol and zinc sulfate were purchased from Macklin Biochemical (China). Sodium sulfate, sodium hydroxide, sodium chloride and ethanol were of at least analytical grade. 18.2 MΩ cm water was prepared with a Center-EDI 60D water purifier (China).

2.2. Fabrication of CFZ and CFZ-steel
100 mL of 1.0 mol L⁻¹ ZnSO₄ solution and 160 mL of 0.5 mol L⁻¹ NaOH solution were successively added to a container with stirring. Zn(OH)₆ was obtained followed by oscillation and centrifugation. Subsequently, 150 mL of 0.8 mol L⁻¹ catechol and 60 mL Zn(OH)₆ were transferred on a water bath. The pH value of mixed solution was adjusted to 9 with diluted NaOH. The reaction was conducted at 70 °C for 1.5 h to obtain the CFZ products.

20# carbon steel (as matrix material) was polished with sandpaper, and then put into ethanol by ultrasonic excitation. Electrodeposition experiments were carried out with constant current mode (-150 mA, 10 cm²) on a stirrer whose rotating speed was 800 rpm. It was measured for 30 min in 60 g L⁻¹ electrolyte (CFZ mixed with Na₂SO₃). SCE was used as reference electrode, and sheathed with Teflon to expose to the electrolytic solution.

2.3. Characterizations
TEM image of CFZ was observed whose accelerating voltage was 200 kV. SEM was used to observe the microstructure of CFZ-steel. The surface area was calculated from nitrogen adsorbent at 77.4 K following standard BET.

Neutral salt spray test was carried out to simulate a gaseous environment. After removal of stains on the specimen surface, the steel plates were hung in a salt spraying machine. These were then continuously sprayed using 50 g L⁻¹ of NaCl solution (pH = 6.5) for 160 h, of which the salt fallout rate was 0.025 mL cm⁻² h⁻¹. After the trail, the steel plates were taken out and gently washed with flowing cold water. When they were dried at 80 °C for 30 min, the rust spot size and corrosion degree of the specimens were further observed.

3. Results and discussion

3.1. Distribution fractions of catechol and Zn at different pH values
The acid-base dissociation of catechol consists in aqueous solution (pKₐ₁ = 9.45), and C₆H₄(O⁻)OH will continue to be dissociated to C₆H₄(O⁻)O⁻ (pK₂ = 12.8). The dissociation process of catechol is presented (Figure 1), and the ion distribution state (δ) of catechol at different pH values is shown in Figure 2. The molecular form is neutral compound when pH is <8. δC₆H₄(OH)OH decreases when pH tends to be 11, and its δ declines to 1/50. δC₆H₄(O⁻)OH ranges from pH 8 to 14, and the maximum value appears at pH 10–12. In addition, C₆H₄(O⁻)O⁻ is dominated after pH >13, and coexists with C₆H₄(O⁻)OH when pH is 12.7.

![Figure 1. Configuration graph of catechol in aqueous solution.](image-url)
Figure 2. Distribution state of catechol at different pH values.

Zn$^{2+}$ in aqueous solution has different forms with the increase of pH value. Since Zn is an amphoteric metal, it dissolves in alkaline solution with hydrogen-oxygen coordination compounds. The form of Zn$^{2+}$ in acidity is based on conditional stability constant ($K$) and cumulative stability constant ($\beta$) as listed in Equation (1). Figure 3 shows the $\delta$Zn under different pH conditions plotted by numerical calculations. The neutral and acidic solutions are in the form of Zn$^{2+}$ when pH is <8, and its $\delta$ is >96.4% with pH 0–8. Zn(OH)$^+$ is an intermediate transition form in aqueous solution whose $\delta$ is <10%. Zn(OH)$^-$ distributes at pH 8–14, and its $\delta$ increases after pH 8.6, reaching 92.6% at pH 11.3. When the solution tends to be more alkaline, Zn(OH)$^{3-}$ converts to Zn(OH)$^{4-}$ after pH >11. Thus, a combined Figure 1 to 3 approach at pH 9 was used to assess the electrodeposition of CFZ on carbon steel.

\[
\begin{align*}
\text{Zn}^{2+} + \text{OH}^- &= \text{Zn(OH)}^+ & \log K_1 &= 4.4 \\
\text{Zn}^{2+} + 2\text{OH}^- &= \text{Zn(OH)}_2^- & \log \beta_2 &= 10.1 \\
\text{Zn}^{2+} + 3\text{OH}^- &= \text{Zn(OH)}_3^2- & \log \beta_3 &= 14.2 \\
\text{Zn}^{2+} + 4\text{OH}^- &= \text{Zn(OH)}_4^{2-} & \log \beta_4 &= 15.5
\end{align*}
\]

Figure 3. Distribution state of Zn(II) at different pH values.
3.2. Morphology of CFZ and CFZ-steel

CFZ products were nanosized crystallines with partly aggregation in TEM examination (Figure 4A). The N$_2$ adsorption-desorption isotherm of CFZ was supplemented (Figure 4B). BET was used to investigate the specific surface and pore volume. The specific surface area of CFZ was determined to be 194.1 m$^2$ g$^{-1}$, and the pore volume was 0.28 cm$^3$ g$^{-1}$. The amount of deposition increased with time, and SEM revealed that 30 min treatment of electrodeposition resulted in carbon steel surface with a lamellar structure whose coatings were compact (Figure 4C), which was caused by the spatially uneven sedimentation of CFZ.

![Figure 4. TEM image (A) and N$_2$ adsorption-desorption (B) of CFZ, and SEM image (C) of CFZ-steel.](image)

3.3. Corrosion resistance performance of carbon steel and CFZ-steel

Corrosion resistance of carbon steel and CFZ-steel were conducted using neutral salt spray test. Surface appearance and corrosion rate of the steels were investigated. Photos were taken about testing specimens to quantify corrosion attack on the surface of the carbon steel. Figure 5B and 5D show the micro-area SEM analysis of Figure 5A and 5C marked by dashed circles.

During the 160-h operation, oxygen was reacted with carbon steel, and rust was progressively formed over the steel surface. CFZ-steel exhibited insignificant corrosion, which was observed from the composite coatings with diffusion barrier. The CFZ-steel plates had small rusty areas with matching coatings appeared in the enlarged images.
Figure 5. Surface photos of carbon steel (A,B) and CFZ-steel (C,D) after neutral salt spray exposure for 160 h.

The corrosions of carbon steel and CFZ-steel continually occurred whose growth tendency of corrosion rate decreased with time (Figure 6). Thus, the corrosion degree of carbon steel mainly depended on the exposure atmosphere and contact time. The average corrosion rate of the steel specimens was in accordance with environmental corrosivity category, demonstrating a nonlinear relationship with contact time.

Figure 6. Effect of contact time on corrosion rate of carbon steel and CFZ-steel; error bars represent standard deviations.
4. Conclusion

Overall, the δ of catechol and Zn(II) were calculated at different pH values, and the CFZ complex was obtained at pH 9 with an effective ligand binding. For fabrication of CFZ-steel, CFZ/Na₂SO₄ media were deposited on carbon steel using direct current electrodeposition. After 30 min electrodeposition, CFZ was gathered tightly on the steel plate, improving the corrosion resistance of carbon steel in atmosphere of oxygen and salt spray. The growth tendency of corrosion rate was gradually reduced, demonstrating the relationship between corrosion rate and contact time. Lower corrosion degree of CFZ-steel was observed during the neutral salt spray process, inducing a limited amount of corrosion attack on the steel surface. The results conveyed a tremendous potential for extending the service life of carbon steel, which had practical prospects for the future use of composite coatings on steel.

References

[1] Chandran M, Bapu G 2013 Electrodeposition of nano crystalline zinc from acid bromide bath and characterisation Acta Chimica and Pharmaceutica Indica 3 213
[2] Yang S, Liao H, Xia Z, Lin W 2020 Effects of side-chain polyether additive on zinc electrodeposition from ammoniacal solution International Journal of Electrochemical Science 15 5609
[3] Li K, Zhai X F, Guan F, Wang N, Duan J Z, Hou B R 2019 Preparation, abrasion and corrosion resistance of zinc coating via ultrasonic assisted electrodeposition Corrosion Science and Protection Technology 31 1
[4] Wang J, Chun F 2019 Discussion on influencing factors during the determination of iron content in galvanized coating of zinc-iron alloy by X-ray fluorescence spectrometry Metallurgical Analysis 39 49
[5] Mistri S, Puschmann H, Manna S C 2016 DNA/protein binding, cytotoxicity and catecholate activity studies of a piperazinyl moiety ligand based nickel(II) complex Polyhedron 115 155
[6] Yuan R H, Liu W H, Teng Y J, Nie J, Ma S Z 2015 Detection of ethoprophos using SERS coupled with magnetic Fe₃O₄/Ag composite materials Spectroscopy and Spectral Analysis 35 1276
[7] Tao D L, Zhang H, Cui Y M, Wang Y Z, Zhang K, Sun W Z 2013 Effect of different types of organic alkali on fluorescence properties of terbium complexes using acetyl catechol as ligand Chinese Journal of Luminescence 34 1295
[8] Devereux M, McCann M, Casey M T, Curran M, Ferguson G, Cardin C 1995 Binuclear and polymeric manganese(II) salicylate complexes: Synthesis, crystal structure and catalytic activity of Mn₃(Hsal)₃(H₂O)₄ Journal of the Chemical Society Dalton Transactions 5 771
[9] O’Connor M, Kellett A, McCann M, Rosair G, Howe O 2012 Copper(II) complexes of catechol combining superoxide dismutase mimetic properties with DNA binding and cleaving capabilities display promising chemotherapeutic potential with fast acting in vitro cytotoxicity against cisplatin sensitive and resistant cancer cell lines Journal of Medicinal Chemistry 55 1957
[10] Liu F H, Chung H J, Elliott J A 2018 Freezing of aqueous electrolytes in zinc–air batteries: Effect of composition and nanoscale confinement ACS Applied Energy Materials 1 1489
[11] Cao H M, Wan F, Zhang L, Dai X, Huang S, Liu L, Niu Z Q 2019 Highly compressible zinc-ion batteries with stable performance Journal of Materials Chemistry A 7 11734
[12] Kundu D, Adams B D, Duffort V, Vajargah S H, Nazar L F 2016 A high-capacity and long-life aqueous rechargeable zinc battery using a metal oxide intercalation cathode Nature Energy 1 16119
[13] Yuan R H, Wu T H, Hu T Y, Shi L, Shi J 2020 Application of S-doped TiO₂ photocatalysts in degradation of BTEX from synthetic surfaces IOP Conference Series: Materials Science and Engineering 892 012014
[14] Qian B H, Ma W X, Lu L D, Yang X J, Wang X 2010 Synthesis, characterization, crystal structure and quantum chemistry calculation of an arenedisulfonate bridged Zn(II) coordination polymer Acta Physico-Chimica Sinica 26 610