

Sustainable design of zinc composite coating using alkali-activated technology: Towards long-term corrosion protection for marine steel

Xue-Sen Lv^a, Xiao-hui Zeng^d, Yao-Cong Han^b, Xudong, Zhao^a, Jian-Xin Lu^{a,*}, Martin Cyr^c

^a Department of Civil and Environmental Engineering & Research Centre for Resources Engineering Toward Carbon Neutrality, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong 999077, China

^b School of Chemistry & Chemical Engineering, Guangxi Key Laboratory for Polysaccharide Materials and Modification, Guangxi Minzu University, Nanning 530006, China

^c Laboratoire Matériaux et Durabilité des Constructions (LMDC), Université de Toulouse, INSA/UPS Génie Civil, 135 Avenue de Rangueil, Toulouse 31077 Cedex 04, France

^d Department of Civil Engineering, Hainan University, Haikou 5720228, China

*Corresponding author: jianxin.lu@polyu.edu.hk (J.X. Lu)

Abstract: This study reported an eco-friendly inorganic zinc composite coating for protecting marine steel based on alkali-activated technology, which coupled synergistically with the passivated effect of alkali-activated slag (AAS) and the cathodic protection of zinc dust. The coating was directly coated on carbon steel and exposed to simulated seawater to explore its protective properties. The effect of chemical compositions of AAS on the corrosion protection of steel and the chemical durability of the coating were investigated. Results showed that the zinc-based AAS coating had a passivated ability for steel with chemical bonding with steel by forming a C-A-S-H/C-S-H gel-like layer. Furthermore, the AAS coating guaranteed excellent barrier protection owing to its superior durability, and no obvious steel rust deposits were found after long-term exposure to chloride solution. The concentration of NaOH influenced the protective properties of the passivated film due to the reducing effect of OH groups. The addition of nano-silica in the AAS formed a compacted coating structure, which was beneficial for the long-term passivation process of steel/zinc and improved the cathodic protection efficiency of zinc dust. The loss of alkaline species of pore solution and degradation of the AAS structure were the main failure mechanisms of the coating during the chloride solution immersion. The optimal coating exhibited 3.8 MPa bonding strength, a cathodic protection period beyond 2800 h (2 times more than organic coating), and negligible degradation of AAS coating binder. The AAS-based coating exhibited longer corrosion protection and advantages in durability and sustainability. This study provides new insight into designing sustainable anti-corrosion coating for protecting steel in harsh marine environments.

Keywords: Alkali activated coating; Passivated film; Cathodic protection; Corrosion protection; Life cycle assessment

1. Introduction

Steel structures are one of the most widely used components in engineering (i.e., reinforced concrete, civil infrastructure, and marine concrete), while they are easily damaged in corrosive environments, resulting in numerous economic losses and security accidents¹⁻³. The annual global corrosion cost accounts for ~2.5 trillion USD, equalling 3.4 % of the global gross domestic product (GDP). The economic loss in China due to steel corrosion is estimated at 50 billion RMB annually, approximately 5 % (GDP)⁴. Adopting corrosion protection methods could save the corrosion cost by 20-30 %, despite decades of effort on corrosion protection of steel, research is still on the study to develop innovative technology with highly effective protection.

Coating technology is the most widely used for steel protection due to its low fabrication cost, facile construction process, high sustainability, etc.^{5,6}. Zinc-rich coatings (ZRCs), containing a zinc content higher than 60 wt.% to guarantee the continuous electrical connection of zinc dust in coatings, have attracted significant attention. ZRCs could provide a dual protective mechanism comprised of the cathodic protection of zinc dust and the shielding protection of corrosion products, resulting in a rapid response and self-healing protection capacity^{3,7,8}.

ZRCs matrix are mainly composed of a binder material conglutinated with zinc dust. According to the film-forming binder, ZRCs are commonly divided into organic or inorganic coatings. The application of organic coatings, i.e., epoxy, polyamine-amide, urethane, and vinyl resins, has distinct disadvantages: (i) showing high manufacture cost, as organic polymers are commonly derived from non-renewable petroleum resources and need multiple manufacturing procedures^{9,10}; (ii) releasing numerous pollutants (i.e., volatile organic compounds) during producing and application period, which cause serious threaten to human health and environment^{11,12}; (iii) organic binders commonly show poor corrosion, weathering, and aging resistance, due to their inferior stability of the chemical structure^{7,13}. In addition, the high content of zinc dust would significantly reduce the film-forming and hardened properties of the binder materials, resulting in the formation of local defeats perceived as weak points, which further exert an adverse impact on the mechanical performances, permeability, and corrosion resistance of coating^{1,5}. This would finally lead to inferior long-term protection performance of coatings, increasing maintenance and

repair economic burdens for the protected structure. Moreover, the quick oxidation of zinc dust reduced the cathodic protection efficiency, increasing the replacement frequency of coating, thus relatively enhancing the consumption of coating resources^{1, 14}. With the emphasis worldwide on the development of sustainable and green practices, clean production of ZRCs with long-term high performance has gained increasing attention.

Alkali-activated material (AAM) is an inorganic binder that is produced by incorporating industrial waste (i.e., slag, fly ash) with an alkaline activator (i.e., water glass, NaOH, and KOH).¹⁵⁻¹⁷. Recently, AAS (Alkali-activated slag) has attracted much interest as a film-forming binder for producing coatings (i.e., waterproof coating, decorative coating, and fire resistance coating), because of their apparent benefits on waste recycling usage enabling sustainable productions. In addition, compared to organic systems, AAS binder shows advanced applicable performances: (i) excellent mechanical strength and chemical tolerance, resulting from its compacted C-A-S-H/C-S-H gel structure¹⁸⁻²¹; (ii) AAS gel has a denser micropore structure and higher tortuosity than other inorganic polymers, facilitating the resistance to aggressive ions diffusion^{22, 23}; (iii) excellent isolating capacity for corrosive ions, attributed to the ions binding behavior in the layer space of gel through electrostatic force²⁴⁻²⁶.

Previous works proved that AAS could provide outstanding long-term corrosion resistance for steel because the alkaline species of pore solution in AAS could form an adsorbed gel-like layer over the passivated film of steel and result in a compacting steel-binder interface^{27, 28}. Similarly, AAS could also form passivated films on zinc dust surfaces to obtain a synergistic anti-corrosion enhancement of zinc coating for steel. This may facilitate a better cathodic protection efficiency of zinc dust. Despite AAS exhibiting distinct advantages in steel corrosion protection, most of the published works are focused on using AAS as a concrete material, and no investigation has been reported regarding AAS as a zinc-rich coating (thin film material) for directly protecting steel.

Therefore, this work aims to explore the feasibility of developing a novel inorganic coating for steel corrosion protection by compositing AAS with zinc dust. The comprehensive performances of AAS-based ZRC (i.e., film-forming, durability, and protection properties) rely on the physicochemical characteristics of the AAS binder, which depend on its chemical composition (i.e.,

activators and precursors). The corrosion protection performance and mechanism of the coating were explored by relating the physicochemical interaction between AAS gel and zinc dust. Also, by relating the chemical evolution of AAS binder, the effect of the chemical compositions (i.e., NaOH and nano-silica) of AAS binder on the long-term corrosion performance of zinc dust and steel was investigated. This study is expected to provide valuable insights for developing high-performance AAS-ZRC for protecting marine steel.

2. Materials and experiments

2.1 Materials

Ground granulated blast furnace slag (GGBS, particle size $d_{50}=8.5\ \mu\text{m}$) was obtained from Beihai Chengde Steel Co., Ltd, China. Its chemical composition determined by X-ray fluorescence (XRF) is shown in Table 1. The alkali-activator was a powdered type water glass ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 2.0), sourced from Foshan Zhongfa Water Glass Manufactory, China. Zinc dust (particle size $d_{50}=6\ \mu\text{m}$, zinc > 99 wt.%) was purchased from Fumei Zinc Industry Co., Ltd, China, and its size distribution and SEM image are shown in Fig. 1. NaOH (Analysis reagent) was provided by Guangdong Guanghua Technical Co., Ltd, China. Amorphous nano-silica (specific surface of $150\ \text{m}^2/\text{g}$, particle size between 7-40 nm) was purchased from Aladdin Chemical Agents Co., Ltd.

Table 1 Chemical composition of slag (wt.%)

Composition	CaO	SiO ₂	Al ₂ O ₃	MgO	SO ₃	TiO ₂	K ₂ O	Na ₂ O	Fe ₂ O ₃	MnO
Content	43.30	27.85	13.22	9.95	1.75	1.17	0.60	0.54	0.29	0.13

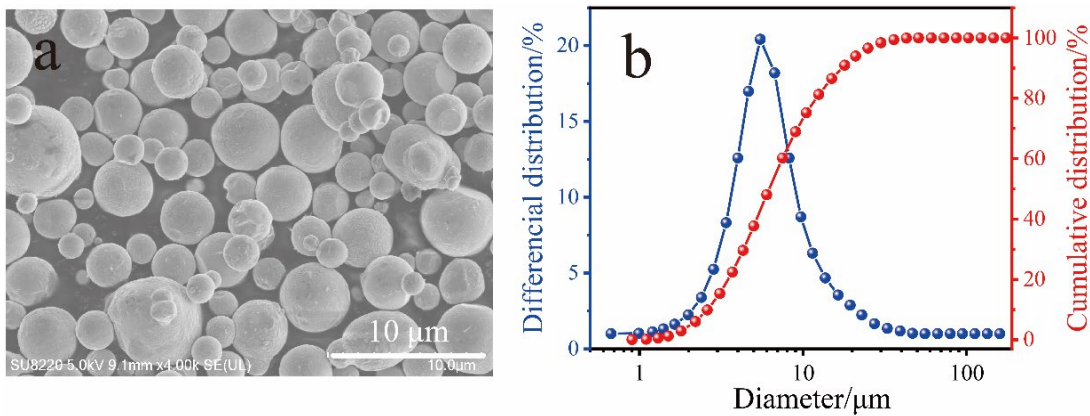


Fig. 1 (a) SEM and (b) particle size distribution of zinc dust

2.2 Preparation of coatings

Fig. 2 shows a powder mixing technology for fabricating the AAS-ZRC coating. The mix proportions of the coatings are shown in Table 2. All the constituents of coatings were mixed in an electrical mixer. Then tap water was added to the well-mixed coating and dispersed homogeneously. The fresh slurry was used as coating and coated on a Q235 steel substrate with a dimension of 30 mm×50 mm. The coating with a dry film thickness of 100 μm was controlled by the weighing method with 0.066 g/cm², which was determined by a preliminary test. The thickness of the coating was evaluated using a film thickness gauge (PosiTector 6000-FN1). The substrate was polished to serve as the calibration surface, and the film difference of the substrate before and after coating was tested and calculated, which was determined as the dry thickness of coating^{29, 30}. Prior to the coating, the steel substrates were sanded and polished using a polishing machine (Buehler AutoMet 250), and then cleaned with ethanol. The coated steel substrates were cured in a chamber at 25 °C and 70 % humidity before properties tests.

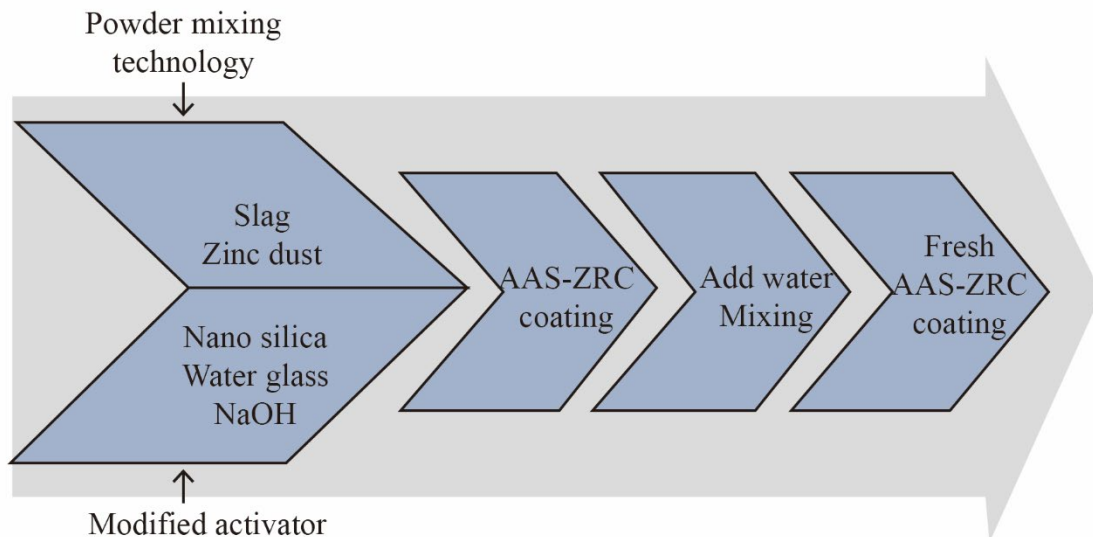


Fig. 2 The fabrication process of AAS-ZRC coating

Table 2 Mix proportions of the AAS-ZRC

Sample	Zn (g)	Slag (g)	Waterglass (g)	NaOH (g)	Nano-silica (g)	Water (g)	Na ₂ O wt. %	Nano-silica wt. %
1#	80	11	13	2.5	/	12	5.20	/
2#	80	11	13	1.5	/	12	4.50	/

3#	80	11	13	0.5	/	12	3.40	/
4#	80	11	13	/	/	12	3.00	/
5#	80	11	13	/	0.32	12	3.00	0.30
6#	80	11	13	/	0.64	12	3.00	0.60
7#	80	11	13	/	0.96	12	3.00	0.90
8#	80	11	13	/	1.28	12	3.00	1.20

2.3 Measurements and Characterizations

2.3.1 Morphology characterization

The coating morphology after 28 d curing was observed using Field Emission Transmission Electron Microscopy (FE-SEM, SU8020, Hitachi) with an accelerating voltage of 15 kV, the elements distribution was mapped by Energy-dispersive Spectrometer (EDS).

3.3.2. Film-forming properties measurements

The bonding strength of the coating was tested by the pull-off method referring to ASTM D7234 using an adhesion testing machine (HCTC-10) after 28 d curing. The surface drying time of the coating was measured according to GB/T 1728-1979. The fresh coating was coated on a steel substrate and cured at 25 °C and 70 % humidity. The surface drying time was determined by a cotton ball blowing through the coating surface without the coating slurry stuck on it. Subsequently, the coating hardened time was obtained as follows, the coating was scratched from the top to the steel substrate, and without coating was adhered to the scratching knife. The hardness of the coating slurry was evaluated according to ISO 1518-1:2002 employing the pencil hardness method. The setting time of the coating slurry was performed following GB/T 1346-2011 using a Vicat apparatus. The average value was reported obtained from three samples for each coating formulation.

2.3.3 Corrosion performance measurements

After 28 d curing, the coating edge was sealed by epoxy resin. The corrosion protection performance of the coating for steel was evaluated by employing an electrochemical workstation (PGSTST 302N). 3.5 wt.% NaCl solution was used as the electrolyte, the coated steel served as the working electrode, and a carbon plate and Ag/AgCl electrode worked as the counter and

reference electrode, respectively.

Open circuit potential (OCP) was conducted after the coatings were immersed in 3.5 wt.% NaCl solution for 12 h to stabilize the electrochemical properties of the coatings. Potentiodynamic polarization was tested with a scan rate of 0.001V/s and a step of 0.001 V, and the corrosion potential and corrosion current density were fitted by Tafel extrapolation method. Electrochemical impedance spectroscopy (EIS) was tested at a frequency between 100 kHz to 0.01 mHz, and the obtained EIS plots were fitted by equivalent electrical circuits using Zsimpwin software.

2.3.4 Corrosion products analysis

The corrosion products of the coating were tested by coating powders, which were scraped from the coating body using a knife. X-ray diffraction (XRD, Rigaku Mini Flex 600) was used to characterize the phase composition of corrosion products of coatings, under a scanning rate of 5°/min, an operating voltage of 40 kV, and a current of 15 mA, respectively. Fourier Transform Infrared Spectroscopy (FT-IR, Thermo Scientific Nicolet, IS 50) was employed to analyze the chemical structure of coatings prepared into KBr pellets in a transmission mode of 4 cm⁻¹ with 64 scanning times. X-ray photoelectron spectroscopy (XPS, Escalab 250Xi) was conducted to analyze the element state and composition of coatings. The X-ray source of Al K α (hv of 1486.6 eV) with a filament current of 16 mA and an operating voltage of 12.5 kV was used. C1s peak of 284.8 eV was used for calibration, and Xpspeak 41 software was applied for high-resolution peak fitting.

2.3.5 Life cycle assessment (LCA) analysis

Life cycle assessment (LCA) was used to evaluate the potential environmental impact of coatings. LCA was conducted by comparing the conventional organic ZRC with AAS-ZRC in the configuration throughout their production-application cycle. The functional unit of the study is set to 1 kg of target coating chemicals used per unit coating area. SimaPro 9.5 and ecoinvent database 3 were used to simulate the production processes of coatings, and the environmental impacts of different coating binders were calculated and compared. The detailed inventory data from the ecoinvent database are listed in [Supporting Information in Table S1 Flow of neat epoxy-ZRC and Table S2 Flow of neat AAS-ZRC, respectively](#). Also, the scope boundaries are illustrated in [Supplementary Information in Figure S1 Diagram of LCA boundary](#). The life cycle impact

assessment was carried out using the TRACI2 protocol to determine the effect of the processes used in this study.

3. Results and Discussions

3.1 Morphology characterization

The micro-morphologies of the coatings containing various contents of NaOH and nano-silica are displayed in Fig. 3. As seen, all coatings showed no cracks while presenting some micro voids in coatings (Fig. 3a-b), and the coating film became denser after adding nano-silica, indicating its pore filling effect (Fig. 3c). Large voids were observed in the cross-section of 1# coating corresponding to its loose structure as shown in Fig. 3d, and the circularity of zinc dust was reduced, implying that zinc dust dissolved and released hydrogen at high alkalinity. In comparison, coating 6# containing nano-silica showed a compacted cross-sectional microstructure with a high circularity of zinc dust encapsulated with dense C-A-S-H/C-S-H gel (Fig. 3e). In addition, larger slag grains were packed with gel due to incomplete depolymerization, but no voids and cracks were observed between the bonding interface of 6# coating/steel (Fig. 3f). The coating was bonded tightly with steel, Fe, Ca, Si and O element gradient distribution with ~500 nm thickness was detected in the bonding interface, suggesting the chemical reaction between gel and steel due to the element diffusion at the bonding interface (Fig. 3g)^{28, 31}. A similar phenomenon was observed at the gel/zinc bonding interface (Fig. 3h). This was attributed to the formation of Zn/Fe-O-Si oxides composited with C-(A)-S-H gel-like layers, indicating that the lattice disruption of metals surface caused by the high alkali oxides of gel which penetrated and deposited in the steel internal^{28, 31, 32}. Results indicated that alkaline AAS coating chemically bonded with and formed a passivated film on the steel and zinc dust.

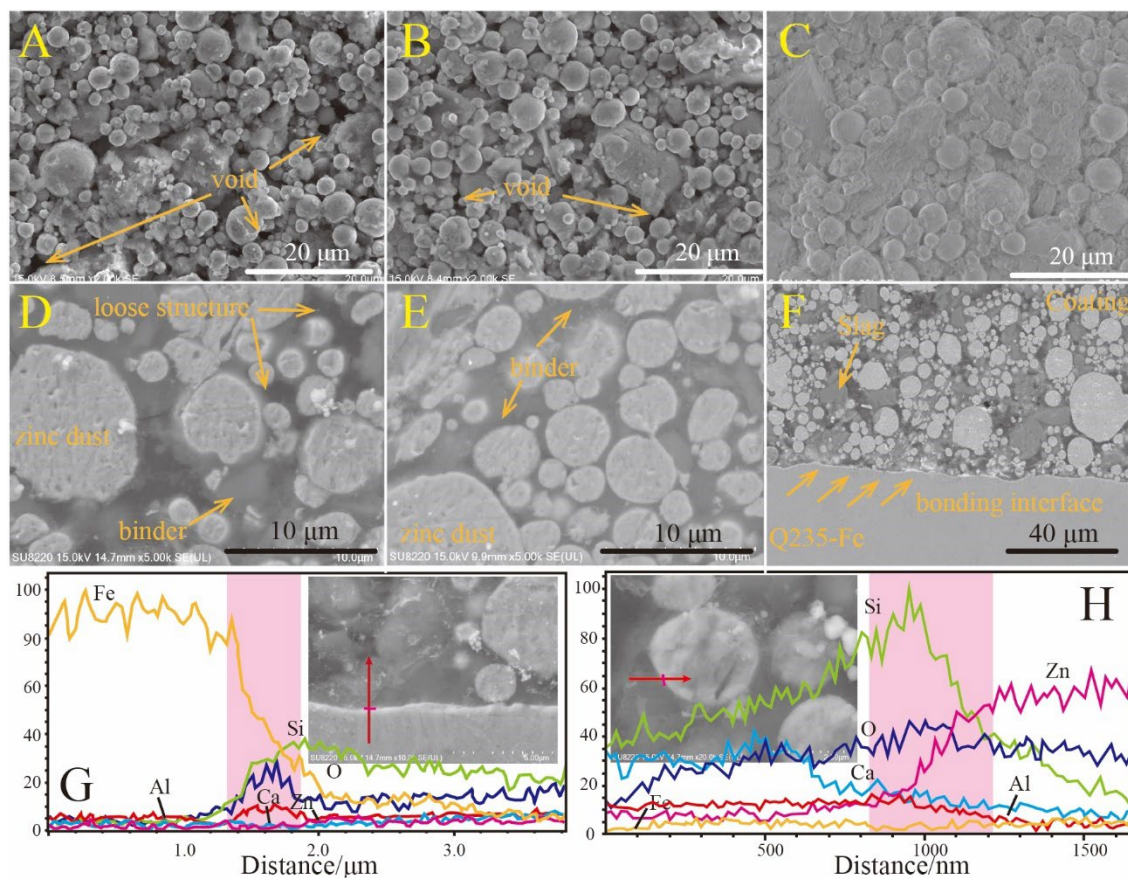


Fig. 3 Surface morphology of coating containing different NaOH and nano-silica contents: (A) coating 1#, (B) coating 4#, and (C) coating 6#; (D) and (E) cross-section of coating 1# and 6#, respectively; (F) bonding interface between coating 6# and steel substrate; (G) and (H) are linear EDS of bonding interface between coating 6# and steel substrate and zinc dust, respectively

3.2 Film-forming properties tests

As shown in Table 3, all of the AAS-ZRCs showed 9 H hardness (the highest grade). Owing to the chemical bonding characteristic of AAS with steel, the bonding strength of coatings ranged from 3.2 to 3.8 ± 0.25 MPa depending on the NaOH and nano-silica concentration, which was much higher than traditional organic coatings (ranged from 1.5-2.5 MPa)^{33, 34}. In addition, the setting time and surface hardened time of coatings ranged from 2.0 to 4.00 h and 64 to 115 min, respectively, which were largely shortened with increasing NaOH addition due to the improving depolymerized degree of slag², while they were slightly decreased with increasing nano-silica concentration because of the accelerating formation of C-A-S-H/C-S-H gels³⁵. The effect of NaOH and nano-silica addition on the surface drying time was less than 20 min due to the fast

water evaporation of the thin coatings. The above results confirmed the successful combination of AAS and high-volume zinc dust (75 wt.% in this study) in preparing AAS-ZRCs with qualified film-forming performances according to the standard of HG/T 3668-2009.

Table 3 The film-forming properties of AAS-ZRC

Sample	Coating hardness (H)	Bonding strength (MPa)	Setting Time (h)	Surface hardened time (min)	Surface drying time (min)
Coating 1#	9	3.5	2.0	64	12
Coating 2#	9	3.6	3.0	75	13
Coating 3#	9	3.3	3.2	86	15
Coating 4#	9	3.2	3.8	96	18
Coating 5#	9	3.3	4.0	101	16
Coating 6#	9	3.8	3.7	103	15
Coating 7#	9	3.5	3.5	108	13
Coating 8#	9	3.2	3.2	115	10
Standard requirement	/	> 3.0	< 5.0	< 120	< 30

3.3 Corrosion protection

3.3.1 Open circuit potential

To evaluate the electrochemical properties of zinc coatings for steel, the open circuit potential evolution of zinc coatings in 3.5 wt.% NaCl solution is exhibited in Fig. 4. The corrosion process of zinc coatings was divided into three stages according to the limit of cathodic protection potential of steel (higher than -780 mV vs. SCE)¹³. At the initial stage I, OCP was shifted negatively due to the activation of zinc dust that resulted from the dissolution of passivated films caused by the penetration of chloride solution into the coating^{7, 13}. In stage II, OCP shifted positively, corresponding to the cathodic protection of zinc dust caused by its corroded dissolution³⁶, and a slower increased rate to -780 mV vs. SCE indicated a longer duration time of cathodic protection. At stage III, the cathodic protection of zinc dust for steel was exhausted when OCP was less negative than -0.780V/SCE³³.

In coating 1#, almost no zinc-activation process was observed. OCP quickly decreased to -1.030V/SCE after 24 h immersion; the potential positively shifted greatly resulting in a cathodic protection period of ~750 h. This suggests the vigorous corrosion process of zinc dust attributed to the absence of the passivated film, resulting from the fast dissolution of zinc dust by high alkalinity of coating, as shown in Fig. 3d. In comparison, OCP in coating 4# decreased negatively

from -0.680V/SCE to -1.052V/SCE corresponding to a zinc-activated time of 72 h, and the cathodic protection period was prolonged to ~1250 h, meaning that the corrosion activity of zinc dust became less vigorous with decreasing alkalinity. Coating 6# showed a longer zinc-activation process of 150 h with a cathodic protection period larger than 2800 h, and the slowly positively increasing rate of the OCP indicated a low corrosion activity of zinc dust. The reason might be the dense microstructure of the coating, and that a passivated film was formed on the zinc dust surface (as shown in Fig. 3e and h), accordingly reducing its corroded dissolution rate and resulting in a higher cathodic protection efficiency. The cathodic protection period of coating 6# beyond 2800 h was much longer than the 1152 h reported from a 75 wt.% zinc-rich epoxy coating³⁴, and performed more like ethyl silicate-based inorganic ZRC³⁷. The results suggest the potential application of AAS-ZRC for corrosion protection of steel in marine structures.

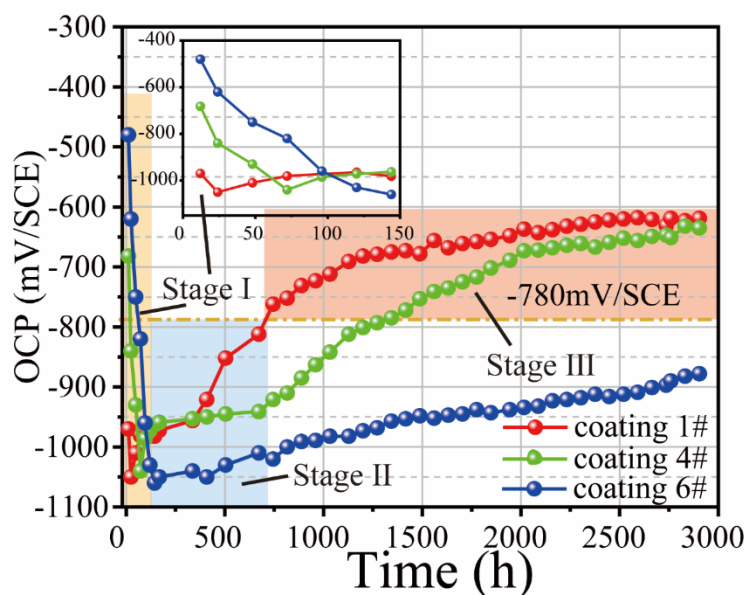


Fig. 4 OCP evolution of the coatings in 3.5 wt.% NaCl solution with immersion time

3.3.2 Potentiodynamic polarization measurement

To analyze the zinc dust electrochemical activities causing cathodic protection, potentiodynamic polarization measurements were conducted and shown in Fig. 5. As shown in Table 4, the R_p value decreased with increasing NaOH concentration, implying the reduction of corrosion resistance of coated steel. With increasing NaOH addition, the E_{corr} shifted positively possibly due to the oxidizing dissolution of zinc dust (as shown in Fig. 3d); The increased I_{corr} value might attributed to the enhancing ionic conductivity because of the higher concentration of Na^+/OH^- ions within

coatings³⁸. Another reason probably is attributed to the increased production of sulphides (HS^- or Sn^{2-}) due to the higher depolymerized degree of slag, since sulphides exhibited a reducing effect which resulted in an increased oxidizing rate of passivated film^{39, 40}. After adding nano-silica, the I_{corr} value of coating 6# was reduced obviously compared with that of coating 5#, which attributed to the compactness of the coating as mentioned in Fig. 3e. As OCP results show, zinc dust provided cathodic protection at this stage. Table 4 shows that the E_{corr} value of coating 6# is slightly lower than that of coating 5#, but R_p value of the former is much higher than that of the latter, demonstrating that the compacted coating structure effectively decreased the oxidation rate of passivated film of zinc dust. However, reduced R_p and increased I_{corr} values were obtained at coating 7# and 8# with nano-silica higher than 0.6 wt.%, suggesting the reduced corrosion resistance of coated steel. This might result from the increased amount of micropores or cracks, which reduced the bonding strength of coatings (Table 3) and the protection performance.

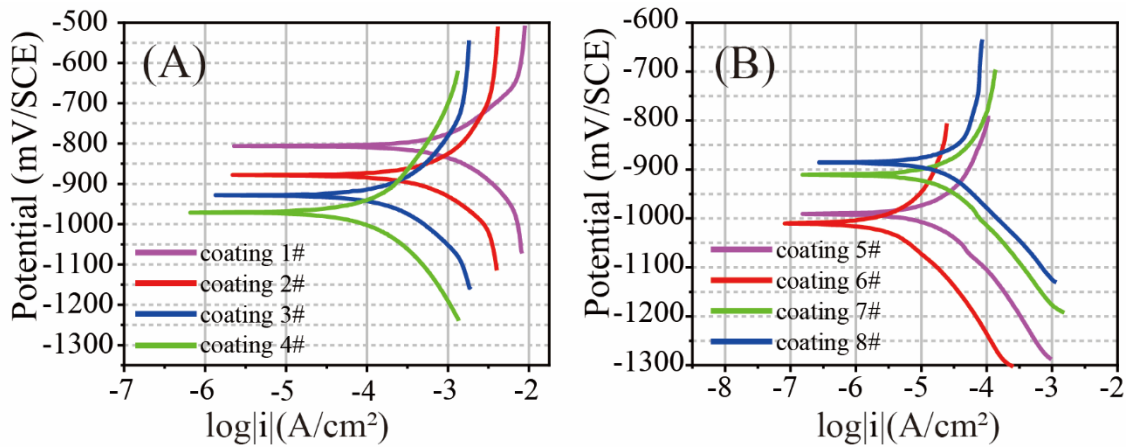


Fig. 5 Polarization curves of coating with different (A) NaOH and (B) nano-silica additions after immersing in 3.5 wt.% NaCl solution for 28 d

Table 4 Fitted results of the polarization curves of the coating

Sample	$E_{\text{corr.}}$ (V)	$I_{\text{corr.}}$ ($\mu\text{A}\cdot\text{cm}^{-2}$)	R_p ($\text{k}\Omega\cdot\text{cm}^2$)
1#	-0.750	2.88×10^2	0.06
2#	-0.873	2.31×10^2	0.27
3#	-0.932	2.19×10^2	0.58
4#	-0.965	8.96×10^1	0.79
5#	-0.987	1.90×10^1	0.97
6#	-1.010	0.98×10^1	1.78

Sample	$E_{corr.}$ (V)	$I_{corr.}$ ($\mu\text{A}\cdot\text{cm}^{-2}$)	R_p ($\text{k}\Omega\cdot\text{cm}^2$)
7#	-0.920	1.15×10^1	1.54
8#	-0.881	1.66×10^1	1.31

3.3.3 Electrochemical impedance spectroscopy

To analyze the effect of NaOH addition on the corrosion resistance of AAS-ZRC, electrochemical impedance spectroscopy (EIS) tests were conducted. As shown in Fig. 6, the capacitive loop in the Nyquist plots decreased with increasing NaOH addition, indicating the decreased resistivity of coating in higher NaOH addition. On the other hand, after 1 d immersion for activating zinc dust, the capacitive loop of coating at fixed NaOH addition increased with time, implying the different protective mechanisms of AAS-ZRC. The protective mechanism was closely related to the surface stability of the passivated film of zinc dust, and the density and uniformity of the steel-matrix interface^{2, 32, 41}. This could be indicated by the evolution of the numbers and location of phase angle in the Bode plots. As seen in Fig. 6, the overlapped phase angle in the frequency region (10^{-2} - 10^3 Hz) was associated with the dissolution of zinc dust and passivated film of steel, which was caused by the corrosion oxidation of electrolytes^{3, 31}. The high-frequency region (10^3 - 10^5 Hz) suggested the increased impedance modulus of coatings. This is because the accumulated corrosion products sealed the micropores within the coating⁴²⁻⁴⁴. Therefore, the alkalinity of the coating influenced the mass and ions transfer between zinc dust and steel, which may induce different protective mechanisms of AAS-ZRC after exposure to aggressive environments. The related mechanisms will be explicated in the following discussion.

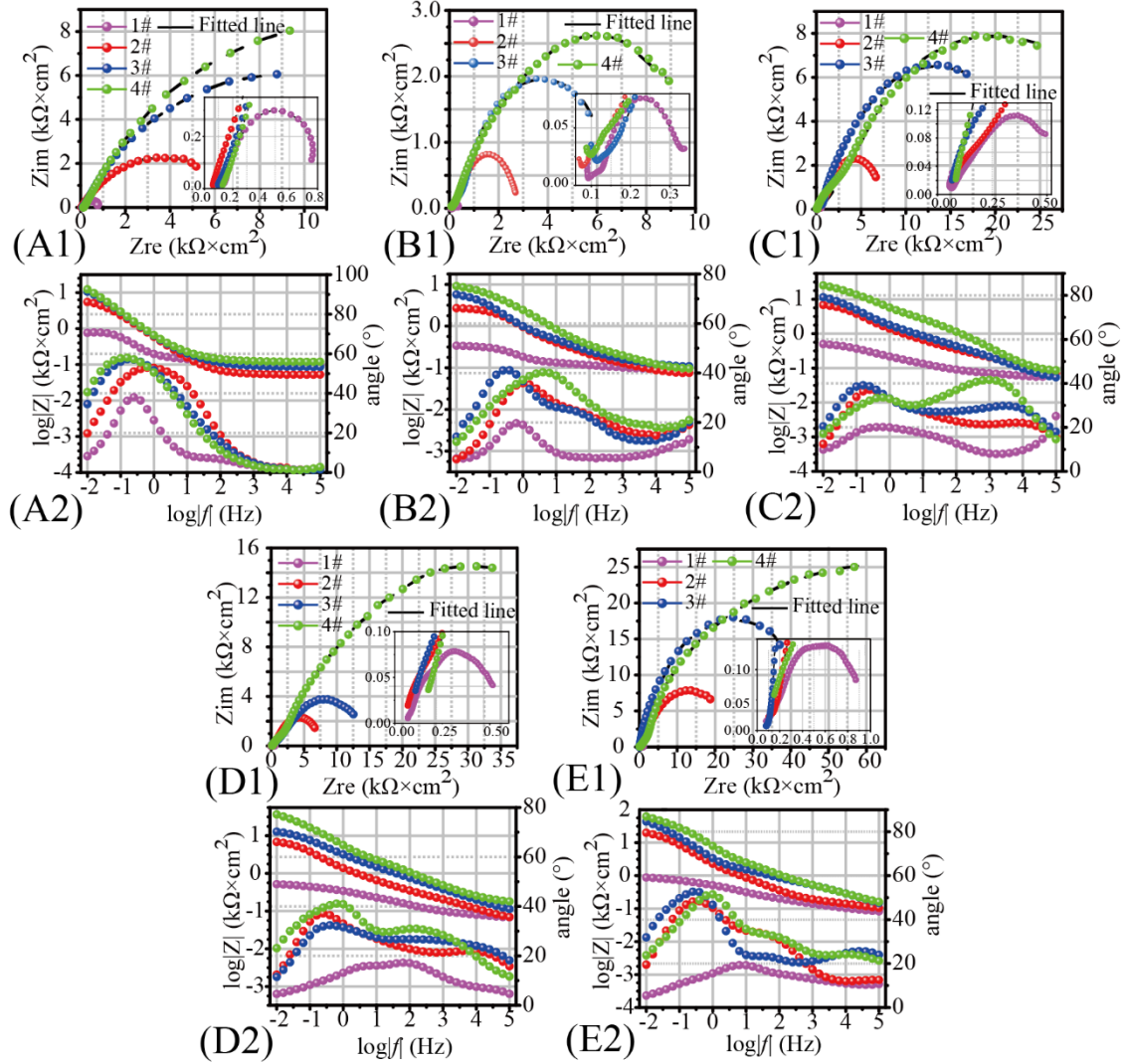


Fig. 6 EIS evolution plots of the coating with different NaOH addition over time (A1) (B1) (C1) (D1) (E1) are Nyquist plots for 1 d, 7 d, 28 d, 56 d, and 90 d, respectively, (A2) (B2) (C2) (D2) (E2) are corresponding to their Bode plots

According to Bode plots in Fig. 6, an equivalent electrical circuit (EEC) with three-time constants corresponding to the three-phase angles was used for EIS fitting^{45,46}, as shown in Fig. 7. The high-frequency time constant (R_cC_c) was associated with the characteristics of coating substrate, and the R_c was the resistance of the coating and C_c was the capacitance of the coating. The medium-frequency time constant (R_pQ_p) was related to the passivated films formed on the steel interface, and the low-frequency time constant ($R_{ct}Q_{dl}$) contributed to the charge transfer process due to the cathodic protection of zinc dust. Constant phase element (CPE) was used to denote the nonideal

behaviour of capacitors^{12, 28, 47}.

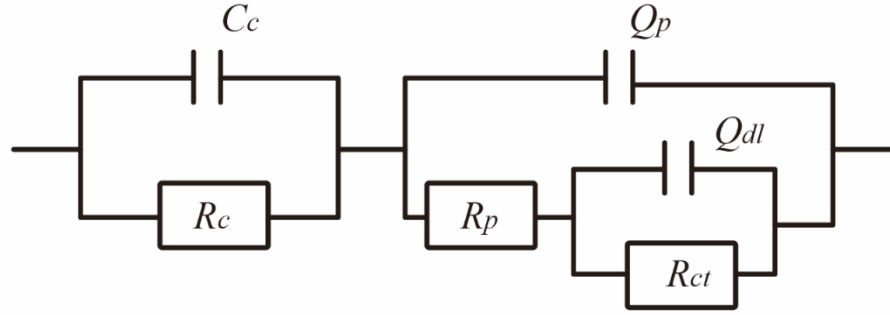


Fig. 7 Equivalent electrical circuits (EEC) used for fitting the EIS plots

The fitted EIS parameters of coatings containing different NaOH additions after long-term exposure to chloride solution are shown in Fig. 8. In general, the R_c value decreased with increasing alkali content due to the increased ions concentration of Na^+/OH^- , which was in line with the results in Fig. 5a. The lower R_p value at higher NaOH concentration indicated the less protective passivated film formed at the steel/coating bonding interface^{28, 48}. The corrosion resistance of steels can be comprehensively evaluated by composing values of R_p and R_{ct} . Although AAS-ZRC exhibited additional R_p value by forming gel-like passivated films at steel, the R_p value was much lower at higher NaOH concentrations, which was indicative of the lower protective properties of the passivated films of steel. Accordingly, the decreased R_{ct} and increased Q_{dl} value with increasing NaOH addition suggested the decrease of double-layer thickness and increase of local dielectric constant of zinc dust, indicating the reduced corrosion resistance of coating due to the fast cathodic dissolution rate of zinc dust⁴⁹.

With prolonged immersion in chloride solution, the rapid increase of R_c value resulted from the blocking effect of corrosion products of zinc dust in the voids of the coatings^{5, 50, 51}. Notably, the increased R_p value indicated an enhanced effect for the passivated film of steel, which might be due to the formation of a compacted gel-like layer at the steel interface resulting from the continuous adsorption of Ca, Si, Al, and corrosive Zn^{2+} ions^{31, 46, 52}. The increased rate of R_{ct} and Q_{dl} were much more pronounced at higher NaOH addition during immersion, indicating the unexpected reduction of corrosion resistance of zinc dust, corresponding to the shorter cathodic protection period of zinc dust. Therefore, the three-phase angles appeared earlier at higher NaOH addition, resulting from the formation of new interfaces originating from the deposited corrosion products (Fig. 6).

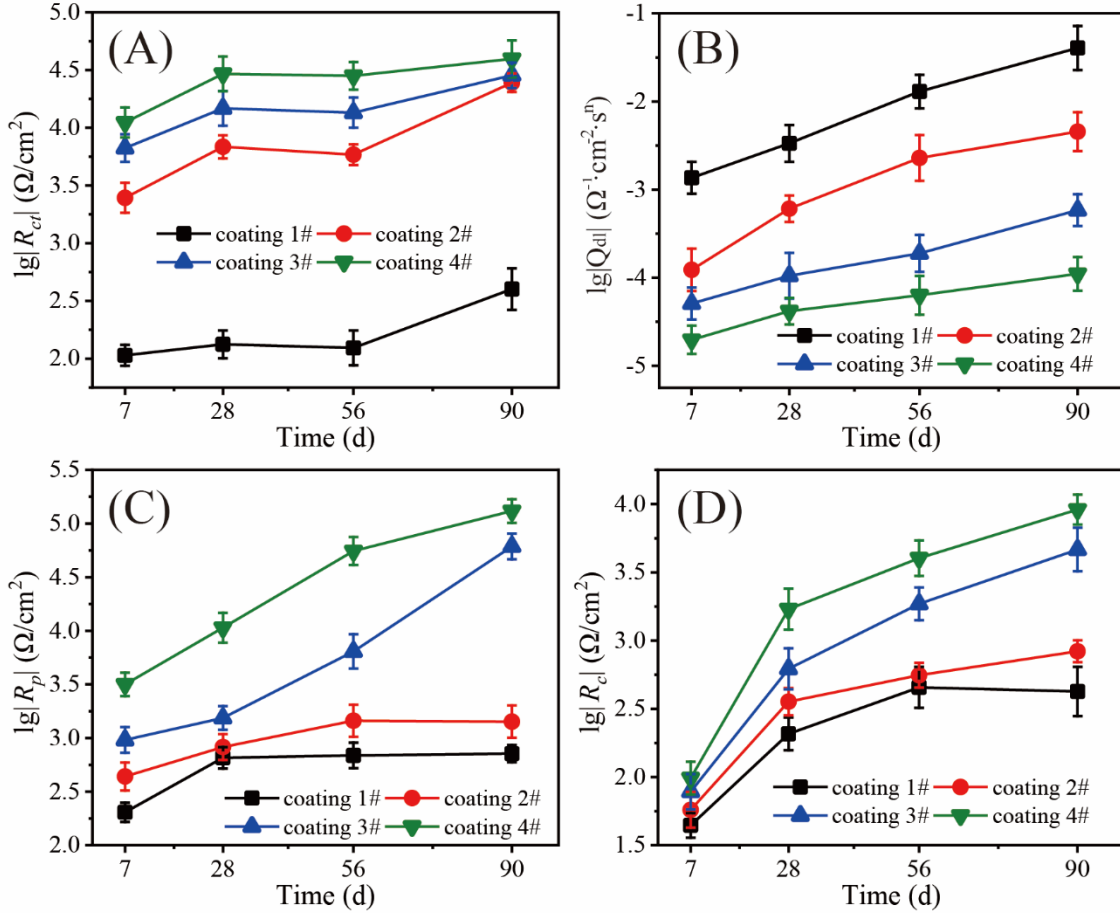


Fig. 8 Fitting results of EIS plots of coatings with different NaOH additions, (A) R_{ct} value evolution, (B) Q_{dl} value evolution, (C) R_p value evolution, and (D) R_c value evolution, $\text{Chi-squared} < 10^{-3}$

Compared with Fig. 6, similar tendencies of Nyquist plots of coatings containing various nano-silica additions could be found with chloride immersion (Fig. 9). However, the overlapped phase angle of coatings presented at low-frequency and medium-frequency was enlarged to 10^4 Hz, which represented the combination of ions transfer resistance and coating resistance^{46, 53}. Moreover, no obvious peak was observed in the high-frequency region (10^3 - 10^5 Hz) in the earlier immersing time, implying a slower deposition rate of corrosion products in the coatings. Thus, EEC with two-time constants shown in Fig. 10 was used to fit EIS plots, which was also used in a similar work¹. The overlapped broad phase angle suggested that the coating was dense and closely bonded with steel^{46, 53}. Accordingly, the transfer of aggressive ions between the coating and passivated film was uniform^{32, 41}. The low-frequency time constant ($R_{ct}Q_{dl}$) noted the charge transfer process of zinc dust, and the higher frequency time constant (R_cQ_c) was associated with

the coating resistance composited by the passivated film, corrosion products or possible precipitation within the coatings^{31, 46}. Constant phase element (CPE) was used to denote the nonideal behaviour of capacitors due to the heterogeneous surface^{1, 5}.

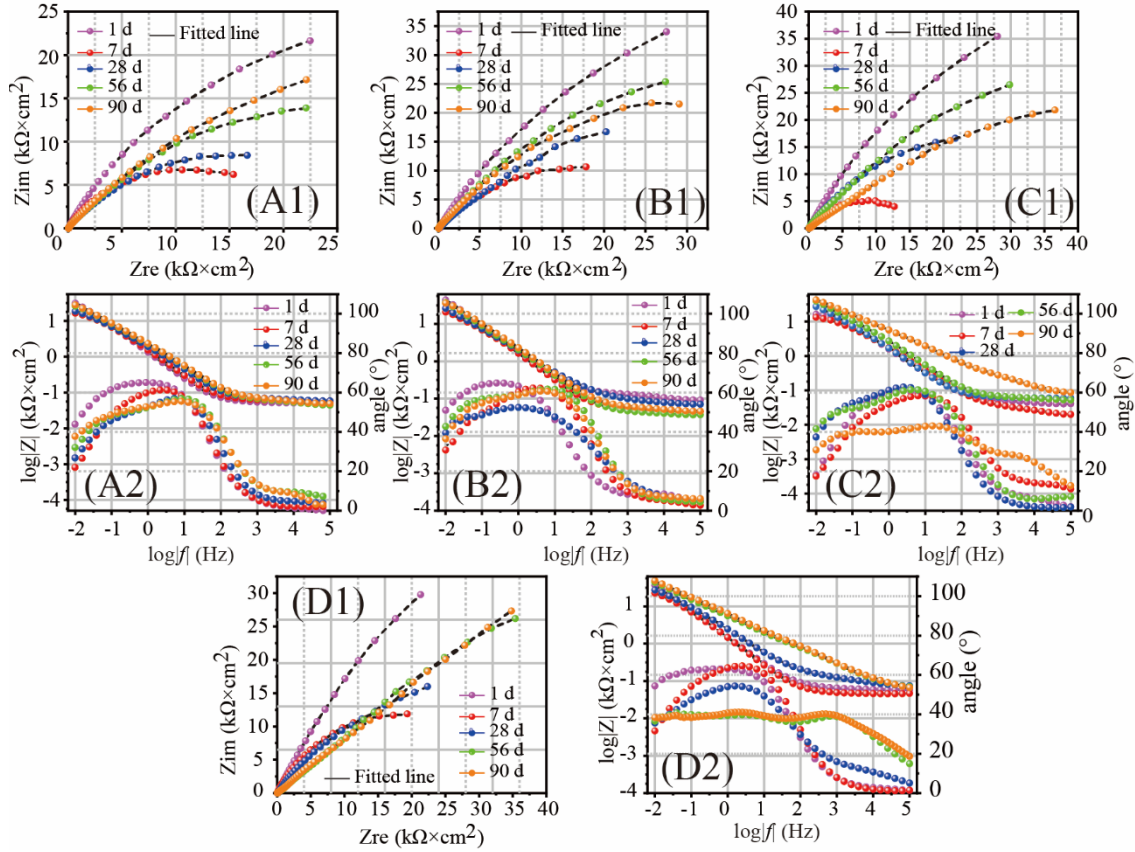


Fig. 9 EIS evolution plots of the coating with different nano-silica additions over time: Nyquist plots (A1) 5#, (B1) 6#, (C1) 7#, (D1) 8#; Bode plots (A2) 5#, (B2) 6#, (C2) 7#, (D2) 8#

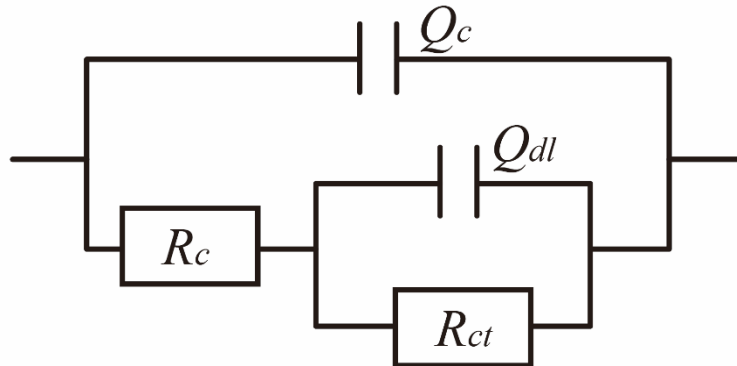


Fig. 10 Equivalent electrical circuits (EEC) used for fitting the EIS plots of coatings containing different nano-silica additions

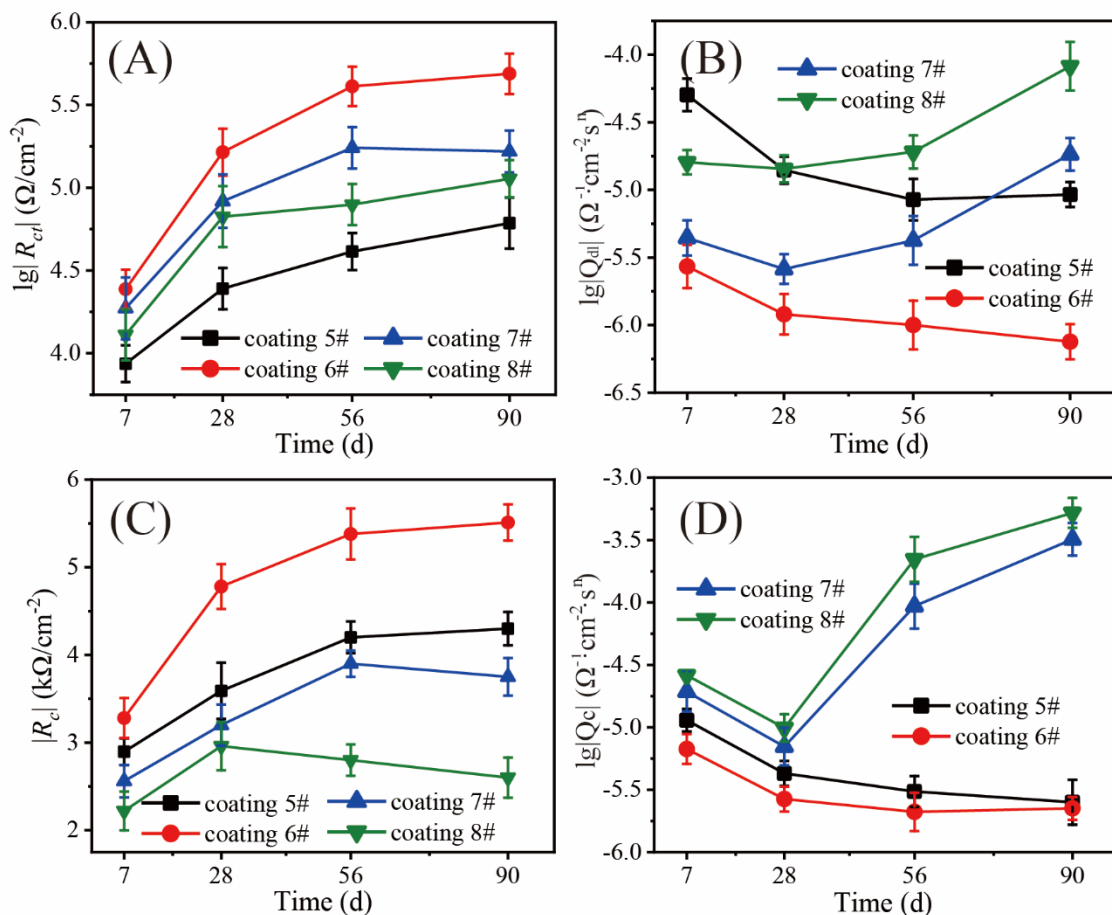


Fig. 11 Fitting results of EIS plots of coatings with different nano silica additions, (A) R_{ct} value evolution, (B) Q_{dl} value evolution, (C) R_c value evolution, and (D) Q_c value evolution, $\chi^2 < 10^{-3}$

The fitted parameters of EIS plots obtained from coating containing various nano-silica additions are shown in Fig. 11. The R_{ct} value of coating increased then decreased with nano-silica addition, and reached the highest value with the lowest increasing rate at coating 6# containing 0.6 wt.% nano-silica (Fig. 11a), suggesting the longer cathodic protective property of zinc dust attributed to its slower dissolution degree. This indicated the higher corrosion resistance of zinc dust, attributing to the stability of passivated film at the zinc dust surface in the AAS binder. The addition of 0.6 wt.% nano-silica resulted in the highest R_c and lowest Q_c value, which was indicative of the optimal corrosion resistance due to the fewer ion concentrations within the coating 6#, as demonstrated in Fig. 11c&d, respectively.

On the other hand, the R_c value increased with immersion time, demonstrating the stable presence of passivated films. This is attributed to the stable chemical environment within the coating, as suggested by the stable value evolution of Q_c , which was guaranteed by the compacted microstructure resulting from the blocking effect of zinc corrosion products. However, the R_c value significantly decreased when the nano-silica content was higher than 0.9 wt.%. The reason was that the reduced flowability of the fresh coating increased the porosity and microcracks^{47, 54, 55}, thus increasing the diffusion concentration of chloride ions within the coating, as also confirmed by the increased Q_c value in Fig. 11d (green and blue lines). This accelerated the oxidized dissolution of zinc dust, which was indicated by the increased Q_{dl} value at earlier 56 d immersing time (Fig. 11b). The R_c value of coating 7# and 8# decreased after long-term exposure to chloride solution (Fig. 11c), indicating the defects of the passivated film of steel^{47, 56}. The increasing expanded corrosion products may cause fine cracks of coatings due to, as indicated by the Q_c value in Fig. 11 d. The above results indicated that adding nano-silica was beneficial for enhancing the long-term barrier and cathodic protection of AAS-ZRC.

3.4 Corrosion behavior analysis

3.4.1 Corrosion morphology

Photographs of ZRCs after chloride immersion are presented in Fig. 12. As shown in Fig. 12 (e-g), serious blisters, bubbles, and rust spots were visual on the surface of organic ZRCs due to the dissolution of organic binder, as reported by other works^{43, 57}. In comparison, although many brownish corrosion products were observed on the surface of AAS coating 1#, 4#, and 8# after 90 d chloride immersion, the coatings were intact without apparent cracking, blistering, and delamination. Furthermore, only white colour spots were visual on the surface of coating 6#, which was attributed to the oxidized products of zinc dust^{33, 58}, confirming the cathodic protection of zinc dust after 90 d chloride immersion, as verified by EIS and OCP results. This result indicated that AAS-ZRC exhibited better steel protective properties than traditional organic-based coatings. Combining the EIS analysis results, the reasons could be attributed to the advantage characteristics of AAS-ZRC as follows: (i) the high chemical durability of AAS ensured stable barrier protection by its robust coating structure during long-term aggressive exposure; (ii) the alkaline pore solution of AAS provided passivated film at zinc dust surface (excepted if zinc dust was attacked too rapidly to form H_2 , as a case of coating 1#), therefore enhancing the corrosion resistance of zinc dust and

significantly prolonging the cathodic protection period of coating. (iii) the chemical bonding between steel and AAS gel formed a gel-like adsorption layer at the steel interface, providing an additional protective film to isolate the diffusing aggressive ions.

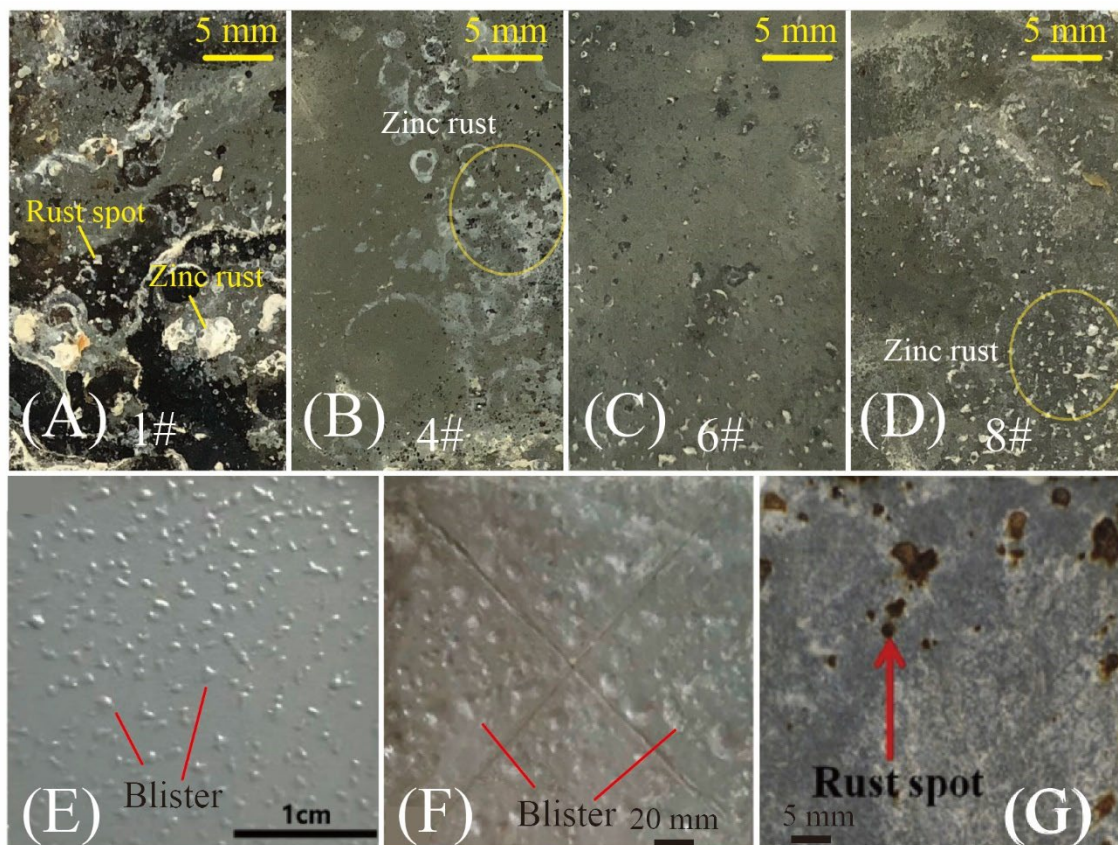


Fig. 12 Photographs of coating surface after immersing for 90 d in 3.5 wt.% NaCl solution (A) coating 1#, (B) coating 4#, (C) coating 6# and (D) coating 8#, (E) 80 wt.% zinc-rich epoxy resin coating surface after being immersed in 3.5 wt.% NaCl solution for 66 d⁴³, (F) 85 wt.% zinc-rich epoxy resin coating surface after being immersed in 3.5 wt.% NaCl solution for 30 d⁵⁷, (G) 80 wt.% zinc-rich acrylic resin coating surface after in 3.5 wt.% NaCl solution for 90 d⁵⁹

The SEM images of the surface of the AAS-ZRC are displayed in Fig. 13. Although rust films and serious corrosion spots were found in coating 1#, the coating surface was still intact (Fig. 13a&b). Instead of the regular shape of zinc dust, a dense layer was coated as barrier protection on the coating surface, mainly consisting of corrosion products of zinc dust (to be discussed in Fig. 15). Dissolving zinc dust and dense layer of zinc corrosion products were observed in coating with lower NaOH addition, indicating the slower oxidation rate of zinc dust (Fig. 13c&d). This result

suggested the dual protection mechanisms of cathodic protection and the barrier effect provided by zinc dust. The oxidation degree of zinc dust was remarkably suppressed, which resulted from the improvement of the compacted structure by incorporating nano-silica (Fig. 13f&e). However, because higher nano-silica additions led to the formation of microcracks due to reducing flowability of coating, the dissolution rate of zinc dust increased, which facilitated the diffusion of aggressive ions (Fig. 13g&h).

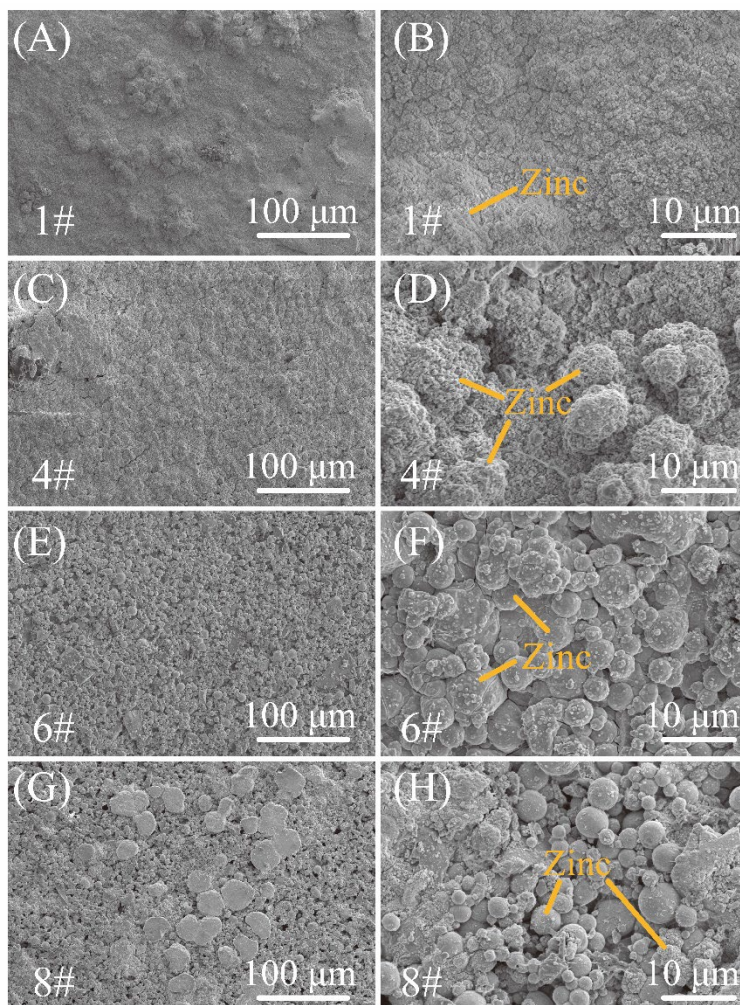


Fig. 13 Coating surface morphology FE-SEM images after immersing in chloride solution for 90 d: (A, B) coating 1#, (C, D) coating 2#, (E, F) coating 6#, (G, H) coating 8#

As seen in Fig. 14, morphologies at the representative steel/coating interface were further detected by FE-SEM/EDS mapping. It was evident that the cross-section structure of coating 1# and 6# were intact and closely bonded with steel, although shorter protection of the coating # was obtained, as shown in EIS results. No corrosion rusts were deposited at the bonding interface. The cross-

section structure of coating 1# was formed by roughly corroded zinc dust, and Cl, Fe, and O elements were distributed at the 1# coating/steel bonding interface, indicating the corroded state of steel and the defects of passivated film. In comparison, uniform distribution of Fe, Cl, and O elements was found at the 6# coating/steel bonding interface, suggesting the highly efficient cathodic protection of zinc dust due to the compacted coating structure provided by nano-silica. This behaviour was in line with the higher R_c and R_{ct} values of EIS results. The results confirmed that: (i) AAS coating could provide excellent barrier protection to suppress the formation of steel rusts within the coating, because of its chemically bonding at steel and the high chemical durability of AAS binder; (ii) although AAS-ZRC was thin, the coating with a compacted structure possessed the ability to maintain a stable passivated film for steel during long-term exposure to aggressive environment.

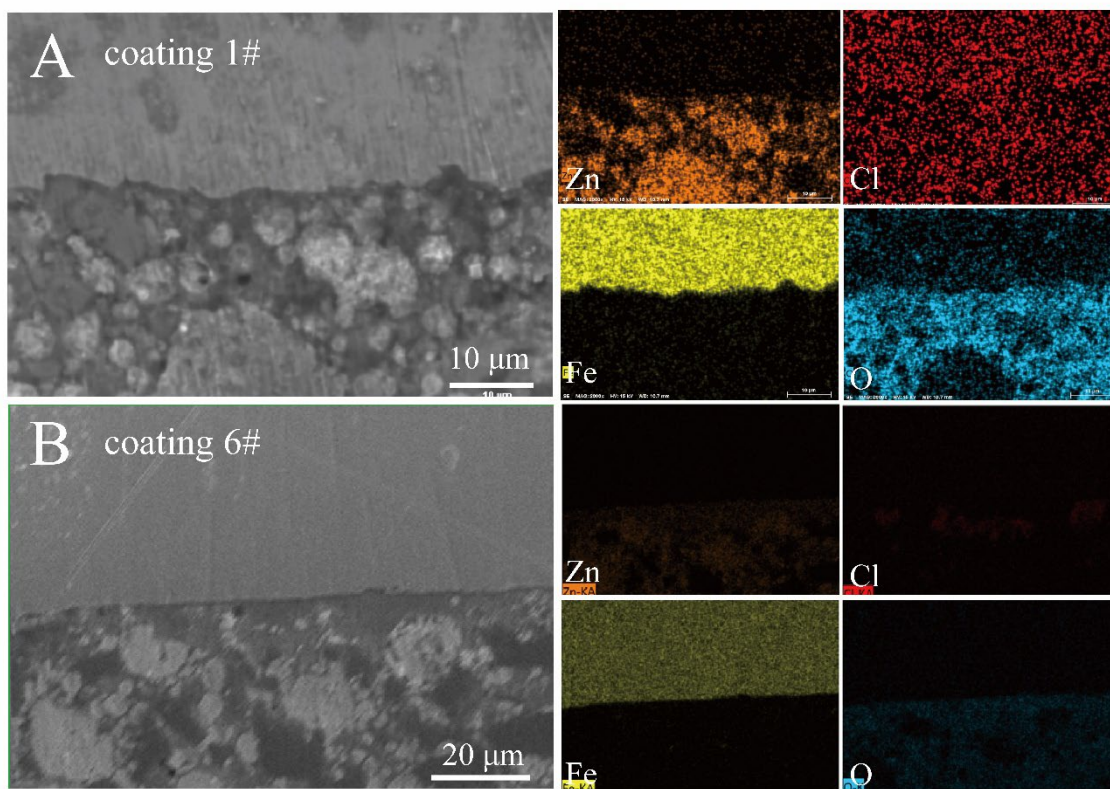


Fig. 14 FE-SEM/EDS of bonding interface of the coating after immersing in chloride solution for 90 d (A) coating 1#, (B) coating 6#

3.4.2 Corrosion products

Fig. 15 shows the chemical compositions of coatings obtained on the coating surface after being

immersed in 3.5 wt.% NaCl solution for 90 d. The corrosion products, generated according to Eq. (1-5), in coating 1# were mainly $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ (after carbonation in the atmosphere) and ZnO. In comparison, zinc was preserved well in coating 6# with a lower oxidation degree, and a weak diffraction pattern of $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$ was detected in coating 6#, indicating its lower intensity and production.

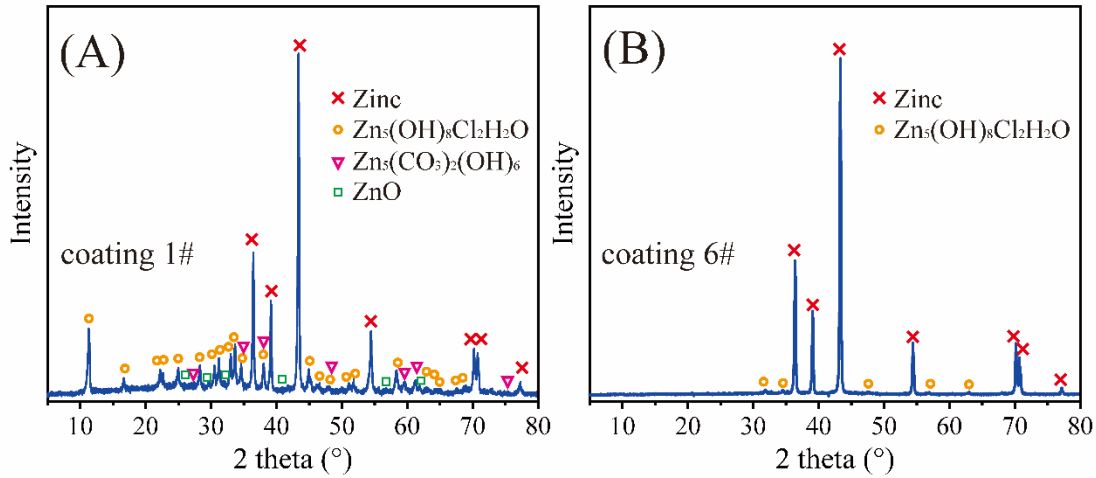
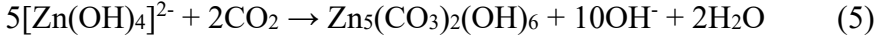
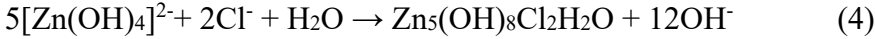
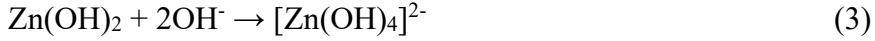
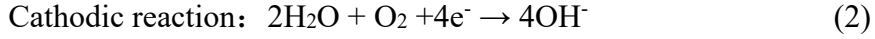
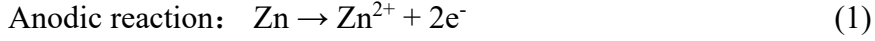


Fig. 15 XRD patterns of (A) coating 1# and (B) coating 6# after immersing in 3.5 wt.% NaCl solution for 90 d

The coating surfaces were also characterized by FTIR, as shown in Fig. 16. The intensive peaks at about 3493 cm^{-1} and 3450 cm^{-1} were attributed to the vibration peaks of the O-H bond, corresponding to a large amount of corrosion product ($\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$) of zinc dust³⁶ in coating 1#, which was consistent with XRD result. 1636 cm^{-1} was assigned to the vibration peaks of the O-H bond of water². Peaks at 1504 cm^{-1} and 1380 cm^{-1} were attributed to vibration peak of $(\text{CO}_3)^{2-}$ groups of $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$ ³³. Peaks at 1038 cm^{-1} represented the vibration peak of Si-O-T (T = Al or Si) of the AAS gel chemical bond⁶⁰. Peaks at 908 cm^{-1} , 725 cm^{-1} , 526 cm^{-1} , and 466 cm^{-1} were corresponded to vibration peak of Zn-OH from $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$ and $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ ^{13, 36}. In comparison, the gel bond Si-O-T in coating 6# appeared at 1018 cm^{-1} , which was much lower

than that of coating 1#, possibly due to the increased content of Si-O-Si bond or the less degradation degree of the AAS gel skeleton^{2, 61, 62}.

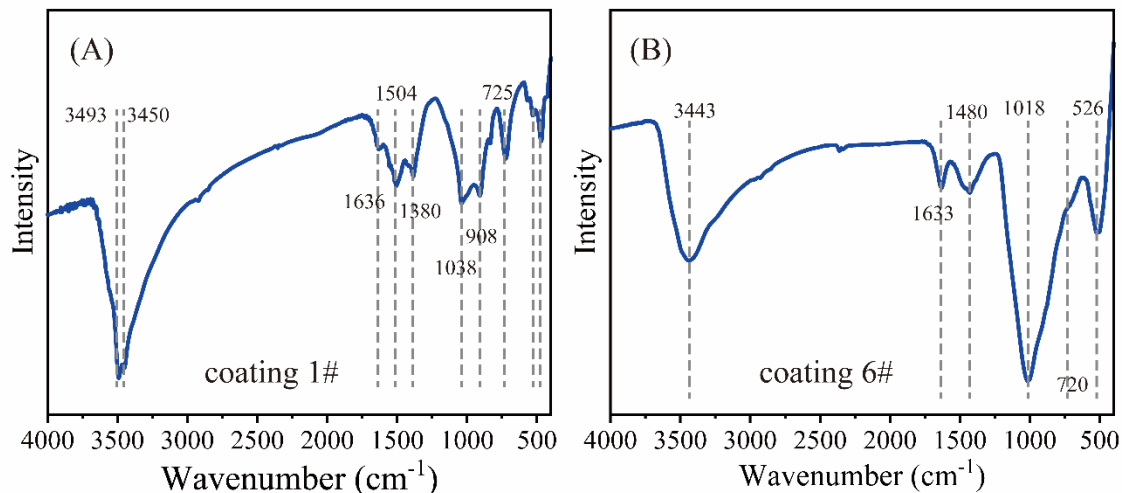


Fig. 16 FT-IR spectra of (A) coating 1# and (B) coating 6# after immersing in 3.5 wt.% NaCl solution for 90 d

To better understand the chemical structure evolution of AAS gel after long-term immersion in chloride environments, XPS results of coatings 1# and 6# are shown in Fig. 17. Si2p spectrum could be divided into two peaks at 102.73 eV and 102.05 eV (Fig. 17a), representing the unreacted aluminosilicate of slag and AAS gel Si-O-T, respectively^{2, 63}. Comparatively, the binding energy and content of Si-O-Si and Si-O-T in coating 1# and 6# were almost the same, indicating the high chemical durability of AAS since its gel skeleton did not change significantly. This result explained the barrier protection of coating 1#, although the cathodic protection of zinc dust disappeared at 28 d chloride immersion (Fig. 4), and the coating preserved an intact structure without cracking, blistering, and delamination after 90 d immersion (Fig. 12). Furthermore, the O1s spectrum peaks of coating 1# at 532.30 eV, 531.66 eV, and 530.94 eV were assigned to the Si-OH presented in the AAS gel structure, the bridging oxygen bond of the AAS gel skeleton (Si-O-Si), and the non-bridging oxygen bond at the terminal of the AAS gel that directly contacted with pore solution (Si-O-Na)^{63, 64}, respectively. Comparatively, the content of the non-bridging oxygen bond in coating 6# was higher than that of coating 1#, confirming the filling effect of nano-silicate. Notably, the Si-O-Na content in coating 1# was significantly lower (21.96 %) than that of coating 6# (38.77 %). This indicated that chloride ions diffused into the gel structure of coating 1#^{2, 63, 64}, resulting in the loss of the alkaline characteristic of the pore solution and causing the chemical degradation of the

gel structure. This further resulted in the defeat of the passivation film at the 1# coating/steel bonding interface.

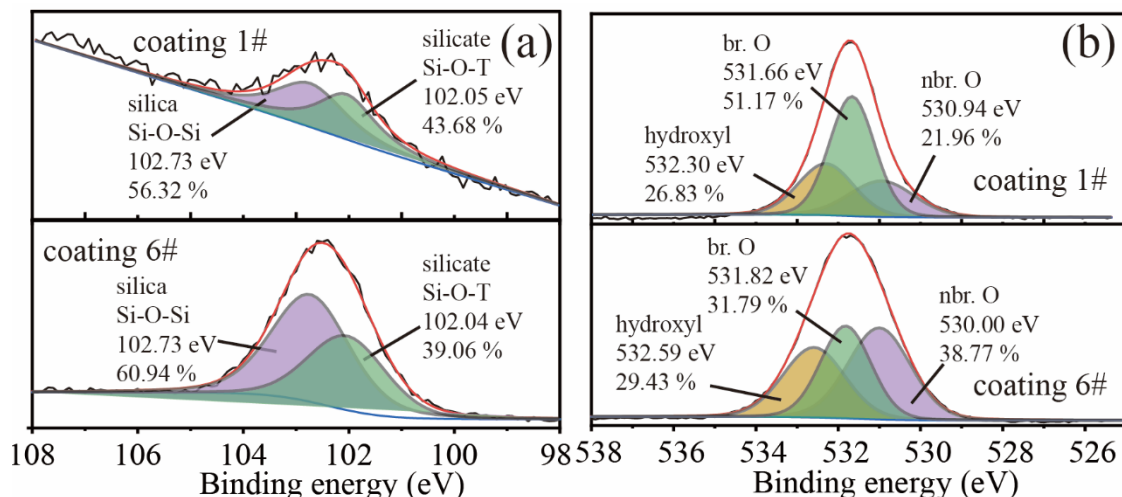


Fig. 17 (A) Si2p and (B) O1s XPS high-resolution spectrum of coating 1# and 6# after immersing in 3.5 wt.% NaCl solution for 90 d

4. Further discussion

4.1 Protection mechanism

The above experimental results verified the possibility of AAS-ZRC for protecting marine steel, which possessed significant advantages in a facile application method and environmental protection compared with galvanizing zinc coating, as can be seen from Fig. 2. Also, Fig. 12 proved that the corrosion resistance of well-designed AAS-ZRC could be much better than that of traditional organic coatings. This was attributed to the formation of the protective passivated film formed at the steel and zinc dust surface by the alkaline pore solution in the AAS and the high chemical durability of AAS gel in corrosive environments, as verified in Fig. 3 and Fig. 14. The results of representative coating 1# and coating 6#, as plotted in Fig. 15, Fig. 16, and Fig. 17, confirmed that the protective properties of AAS-ZRC were highly dependent on the alkalinity and compactness of AAS coating. Based on these findings, the protective process and mechanism of AAS-ZRC are demonstrated in Fig. 18.

Although passivated films were formed at the steel and zinc dust surface in AAS coating during the passivation stage (Fig. 18a), the coating with high contents of NaOH provided less protection

to steel due to the two negative effects: (i) high dosage of NaOH reacted preferentially with intermediate corrosion product $[\text{Zn}(\text{OH})_4]^{2-}$ and Cl^- to form precipitate $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$ ^{2, 3}, accordingly resulting in short cathodic protection period due to the rapid oxidation of zinc dust (Fig. 15a & 16a). (ii) excessive NaOH accelerated the breakdown of the passivated film because of the high reducing effect of OH^- (Fig. 14a), increasing the risk of chloride-induced corrosion (Fig. 18b1). Thus, coatings 1# with high NaOH inclusion (5.2 wt.% alkalinity) exhibited a low corrosion resistance and a short cathodic protection period in an aggressive environment (Fig. 18b2), with many rust spots deposited on the coating surface after long-term immersing in NaCl solution (Fig. 12a)

It was worth noting that certain alkalinity was essential in the coating to maintain the chemical stability of passivated film at steel surfaces (the optimal alkalinity is 3.0 wt.% in this study)⁶⁵. Moreover, the reduced sulfur (1-3 wt.%) presented in slag readily dissolved in an alkaline environment and transferred into sulfur species (HS^- and S_n^{2-})^{14, 40, 46}, giving a reducing effect on the passivated film. Therefore, competitive adsorption between $\text{HS}^-/\text{S}_n^{2-}$ and OH^- was presented on the surface of the metal, which hindered the growing process of the passivated film (Fig. 18b2)^{46, 66}.

On the other hand, the passivation process was a long-lasting depositing reaction between AAS and metals^{41, 47}. In other words, the thickness and morphology of the passivated film were strongly associated with the internal chemical environment of the AAS binder^{65, 67}. The addition of nano-silica with 0.6 wt.%, as a case of coating 6#, compacted the microstructure of the coating to restrict the diffusion of chloride ions (Fig. 3c), delaying the breakdown of passivated films of zinc dust and prolonging the cathodic protection efficiency (Fig. 18c1). Notably, the compacted microstructure was beneficial for the gradual formation of a compacted gel-like layer on the metal surface by adsorption of AAS pore solution and zinc species corrosion products (Fig. 11c). The abovementioned double positive effect reduced the risk of chloride-induced corrosion.

However, the high nano-silica content (> 0.6 wt.%), as cases of coating 7# & 8#, resulted in micropores, causing the reduction of protection capacity. After long-term exposure to an aggressive environment, the leaching of alkaline species of AAS coating inevitably reduced the

pH value on the metal surface and degraded C-(A)-S-H gels (Fig. 16a & 17a), resulting in the defects of passivated films and the initiation of corrosion spots. However, the highly robust coating structure, owing to the excellent stability of the AAS gel Si-O-Si skeleton (Fig. 16b & 17b), formed an intact coating and tightly bonding interface (Fig. 13b), thereby providing stable barrier protection for steel. Moreover, based on the protection mechanism of zinc dust, after zinc dust achieved cathodic protection, the dissolved Zn^{2+} and OH^- diffused to the coating surface and enriched in the volumetric porosity due to the concentration difference force. The Zn^{2+} and OH^- ions preferentially reacted with Cl^- at the coating/solution contacting interface (Fig. 15 & 16), and deposited solid corrosion products to seal the micropores within the coating (Fig. 13). Finally, a dense layer formed by corrosion products coated on the surface top of the coating, therefore decreasing the porosity of the coating and further promoting its barrier protection efficiency (Fig. 18c2).

The above findings indicated that AAS-ZRC has promising potential to be applied as a coating for protecting marine steel, such as marine reinforced constructions and steel, etc. Distinct advantages of forming passivated metal films and good binder durability for AAS zinc coatings were proved compared with traditional organic-based coatings. The optimal formulation was achieved as follows: alkali-activated Zn-slag system with a 3.0 wt.% alkalinity and 0.6 wt.% nano-silica. However, the alkalinity and micropore structure are two important factors in determining the stability of the passivated film of steel and the cathodic protection efficacy of zinc dust⁶⁸. Hence, in the future, the alkali-activated system will be tailored by different activators and precursors for designing high-performance AAS-ZRC.

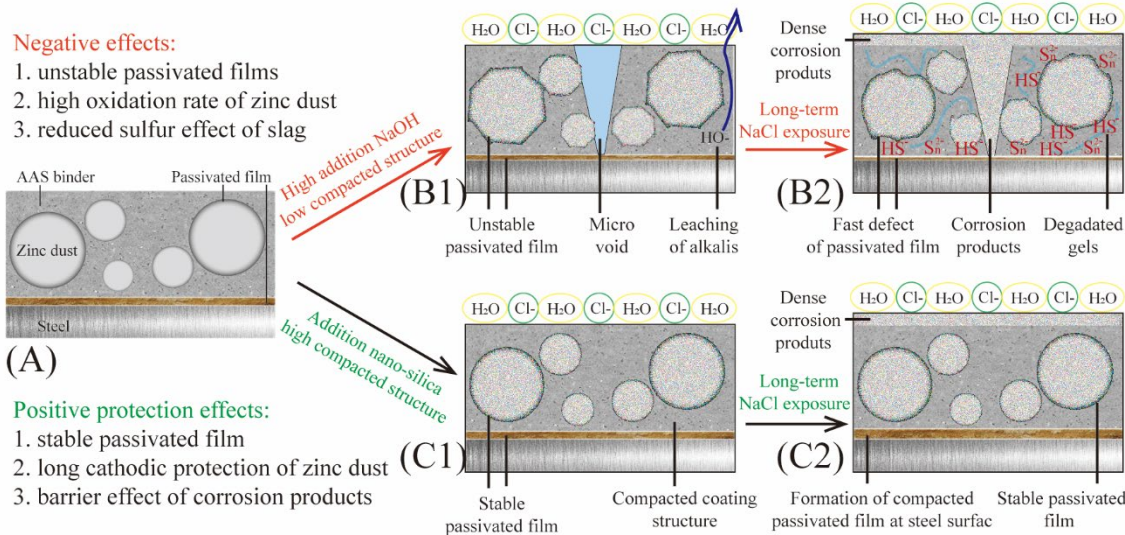


Fig. 18 Schematic diagram of the protection and deterioration mechanism of AAS-ZRC in a long-term chloride exposure environment

4.2 Sustainability discussion

As shown in Table 5, AAS-ZRC exhibited advantageous longer cathodic protection duration than many reported organic polymer-based ZRC, resulting from the superior efficiency of zinc dust due to the passivated effect of alkali AAS gel. Compared to conventional organic ZRC, AAS-based ZRC shows higher coating resistance (Fig. 19a) and charge transfer resistance (Fig. 19b), indicating an exceptional corrosion protection capacity. Percolation is one of the major problems that strongly deteriorate the barrier protection efficiency of conventional ZRCs, resulting from the easy degradation of organic binders in corrosive environments. Furthermore, the local defect with high porosity caused non-uniform consumption of zinc dust, reducing its sacrificing performance.

Table 5 Comparison of the cathodic protection duration of the zinc-rich coatings

Binder	Zinc content (wt.%)	Dry film thickness (μm)	Cathodic protection duration (d)	Reference
Epoxy/polyamide	90	65	25	69
Epoxy/gallate	70	100	25	70
Epoxy/polyamide	85	100	70	71
Epoxy/polyamide	80	100	70	71
Epoxy/polyamide	75	100	40	71
Ethyl silicate	77	60	60	72
Epoxy	78	65	19	73

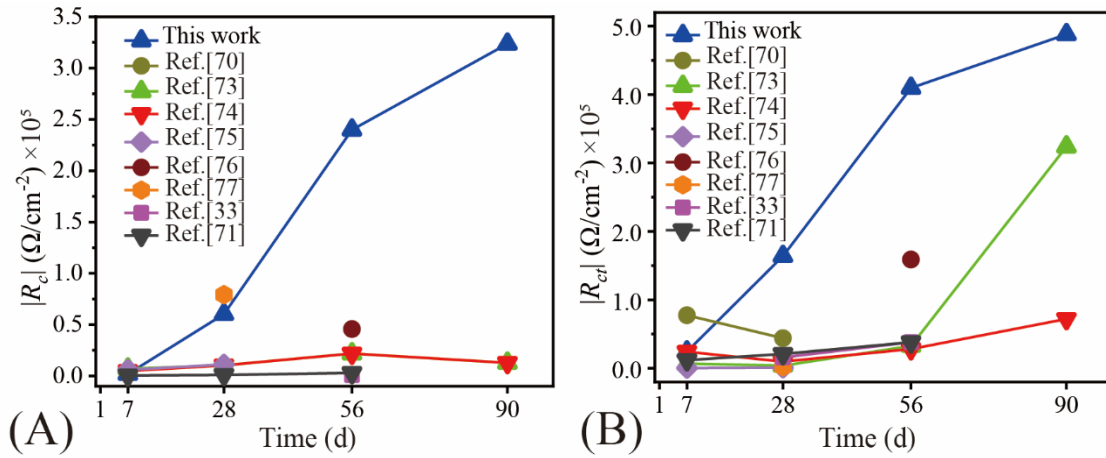


Fig. 19 Comparison of electrochemical impedance parameters of AAS-ZRC and conventional organic ZRC: (a) R_c value, (b) R_{ct} value^{33, 70, 71, 73-77}

Table 6 shows the cost and environmental impact results of the conventional epoxy and AAS-ZRC. For a fixed zinc content, the production cost of AAS binder is ~8 times lower than organic epoxy^{78, 79}. Due to the superior protection of AAS binder, the zinc content can be reduced for designing ZRC at the same corrosion protection performance by using AAS. In other words, the dosage of zinc dust in AAS could be reduced compared to organic ZRC. As the zinc dust (\$4.5/kg) is more expensive than binders, thus using more AAS binder can significantly decrease the coating cost. In addition, AAS-ZRC could positively reduce the impacts on human health and environment. The environmental impacts of AAS-ZRC during its life cycle, i.e., ozone depletion, global warming, smog, acidification, eutrophication, ecotoxicity, and fossil fuels are reduced by 220 %, 56 %, 75 %, 75 %, 72 %, 380 %, and 580 %, respectively. Also, the human health impacts, i.e., carcinogenic, non-carcinogenic, and respiratory effects, decreased by 4.8, 2.8, and 2.1 times, respectively. These benefits are attributed to the reduced usage of hazardous chemicals of organic resin (i.e., epoxy, resin hardener, and other chemical compounds). The corresponding production and utilization of these chemicals are the main processes contributing to the environmental impacts in the LCA.

Table 6 Cost and LCA comparison between epoxy ZRC and AAS-ZRC.

Impact items	Unit	Epoxy ZRC	AAS-ZRC
Ozone depletion	CFC-eq $10^{-11}/\text{kg}$	2.09×10^{-7}	4.619×10^{-8}

Global warming	CO ₂ -eq/kg	4.580	2.570
Smog	O ₃ -eq/kg	0.425	0.317
Acidification	H ⁺ -eq/mol	1.480	1.100
Eutrophication	N-eq/kg	2.85×10 ⁻²	2.04×10 ⁻²
Carcinogenic	CTUh	1.45×10 ⁻⁶	0.30×10 ⁻⁶
Non carcinogenic	CTUh	1.63×10 ⁻⁵	0.59×10 ⁻⁵
Respiratory effects	PM10-eq/kg	9.47×10 ⁻³	4.68×10 ⁻³
Ecotoxicity	CTUe	476	125
Abiotic depletion, fossil fuels	MJ	59.9	10.3
Binder cost	¥/kg	18.0	2.2

Note: eq mark for equivalent quality

5. Conclusions

This study developed an AAS-ZRC coating for protecting steel subjected to marine corrosion. The effect of alkalinity and nano-silica on the film-forming properties and protection performances of the coating was investigated. In addition, the protection mechanisms for coated steel were investigated during exposure to aggressive environments. The findings and conclusions can be drawn as follows:

(1) The AAS possessed a superior protective ability to coat steel than organic coatings due to the C-A-S-H/C-S-H gels precipitated on the metal surface to form a passivated film, which highly improved the corrosion resistance of steel and prolonged the cathodic protection period of zinc dust beyond 2800 h.

(2) The AAS-ZRC provided barrier protection due to the zinc corrosion products densely coated on the surface top of the coating. The durable C-S-H/C-(A)-S-H of AAS guarantees the barrier protection capacity for long-term corrosion resistance.

(3) Less stable and protective passivated films were formed in coating with high alkalinity (> 3.0 wt.%), resulting in a much shorter cathodic protection period of zinc dust and lower corrosion resistance of steel.

(4) The protective performance of AAS-ZRC was strongly associated with the physicochemical stability of passivated films of steel and zinc dust. Adding nano-silica refined the microstructure of the coating to reduce the diffusion of chloride ions and formed a stable passivated film. However, high nano-silica content (> 0.6 wt.%) increased microcrack risk and decreased protective ability.

(5) The loss of alkaline species of pore solution and degradation of C-S-H/C-(A)-S-H resulted in the breakdown of passivated film. However, compared with organic coatings, AAS coating

showed more long-lasting barrier protection beyond 90 d immersing in 3.5 wt.% NaCl solution.

(6) Compared to conventional organic ZRC, AAS-ZRC showed obvious sustainable advantages in saving costs and protecting environmental and human health, while possessing superior protection properties to marine steel.

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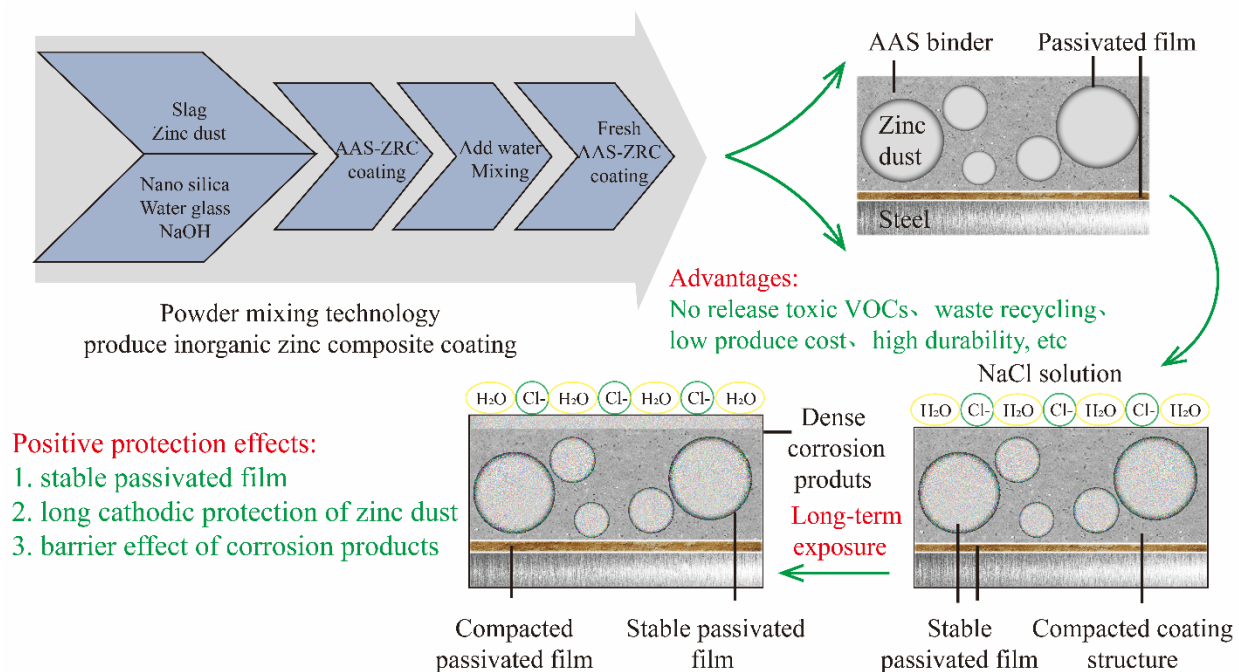
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884 **Synopsis:** using waste slag produces inorganic zinc coating for protecting marine steel with long-
 885 term protective performance and without possessing toxic and hazardous substances

Supporting Information for

Sustainable design of zinc composite coating using alkali-activated technology: Towards long-term corrosion protection for marine steel

Xue-Sen Lv^a, Xiao-hui Zeng^d, Yao-Cong Han^b, Xudong, Zhao^a, Jian-Xin Lu^{a,*},
Martin Cyr^c

^a Department of Civil and Environmental Engineering & Research Centre for Resources Engineering Toward Carbon Neutrality, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong 999077, China

^b School of Chemistry & Chemical Engineering, Guangxi Key Laboratory for Polysaccharide Materials and Modification, Guangxi Minzu University, Nanning 530006, China

^c Laboratoire Matériaux et Durabilité des Constructions (LMDC), Université de Toulouse, INSA/UPS Génie Civil, 135 Avenue de Rangueil, Toulouse 31077 Cedex 04, France

^d Department of Civil Engineering, Hainan University, Haikou 5720228, China

*Corresponding author: jianxin.lu@polyu.edu.hk (J.X. Lu)

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Life cycle assessment (LCA) analysis method

Life cycle assessment (LCA) was conducted by comparing the conventional organic ZRC with AAS-ZRC in the configuration throughout their production-application cycle. The functional unit of the study is set to 1 kg of target coating chemicals used per unit coating area. SimaPro 9.5 and ecoinvent database 3 were used to simulate the production processes of coatings, and the environmental impacts of different coating binders were calculated. The detailed inventory data from the ecoinvent database are listed in Table S1 and Table S2, respectively. Also, the scope boundaries are illustrated

in Figure S1. The life cycle impact assessment was carried out using the TRACI2 protocol to determine the effect of the processes used in this study.

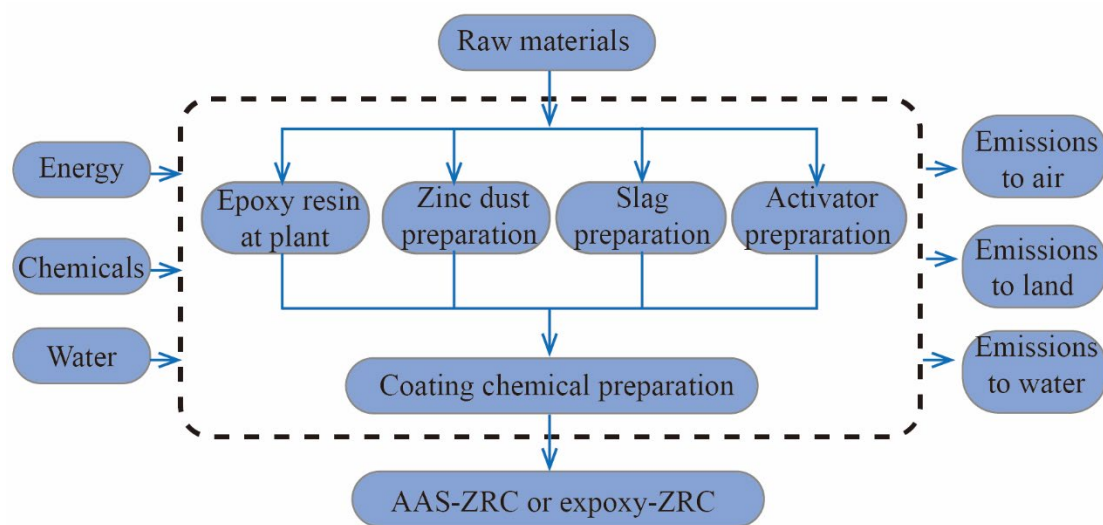


Figure. S1 Diagram of LCA boundary

Table S1 Flow of neat epoxy-ZRC

Flow input	Category	Unite	Amount
Epoxy resin, liquid market for epoxy resin, liquid	Chemicals/organics	kg	2.05
Zinc dust, the market for zinc dust	Metals/no Ferro	kg	4.55
Flow Output	Category	Unite	Amount
Epoxy-ZRC	Chemicals/organics	m ²	1

Table S2 Flow of neat AAS-ZRC

Flow input	Category	Unite	Amount
Zinc dust, the market for zinc dust	Metals/no Ferro	kg	4.55
Ground granulated blast furnace slag, ground granulated blast furnace slag production	Construction/binders	kg	0.626
Sodium silicate, without water	Chemicals/inorganics	kg	0.740
Tap Water	Water/industry water	kg	0.683
Flow Output	Category	Unite	Amount
AAS-ZRC	Construction/binders	m ²	1