Short Communication

Effect of Phosphating and Post-sealing on the Corrosion Resistance of Electro - galvanized steel

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To improve the corrosion resistance of electro-galvanized (EG) steel, the EG steel was initially treated by utilizing the phosphating with phosphate and then sealed by the technique of post-sealing with silicate solution. The surface morphology and elemental composition of the three samples were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The effect of the phosphating and post-sealing treatment on the corrosion resistance of EG steel was investigated by neutral salt spray test (NSS), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. The results showed that, after phosphating, the porous phosphate crystals formed on the surface of the electro-galvanized steel, and additionally, due to the existence of sodium silicate which adequately filled into the phosphate pores, a complete layer of silicate film formed on the phosphate coating, the corrosion resistance ability of EG steel was enhanced further. The phosphating and post-sealing treatment reduced the corrosion current density of EG steel by one order of magnitude, besides, the impedance values were increased obviously. In particular, the anodic oxidation and the cathodic reduction of zinc were inhibited during corrosion process, the active dissolution of zinc was much lower, improving remarkably the corrosion of the EG steel.

1. INTRODUCTION

With the rapid development of modern manufacturing technology, the demand for the electro-galvanized (EG) steel has increased greatly [1-4]. Nevertheless, the EG steel was easily corroded for

being exposed to the air for a long time because of the thin zinc layer and the activity of zinc [5,6]. In order to increase the service life of the EG steel, conversion coating treatment is generally adopted. Typically, chromate treatment was widely used because of it can be easy to operate and can greatly improve the corrosion resistance of EG steel. However, chromate treatment was gradually eliminated, due to the environmental pollution of hexavalent chromium [7,8]. In recent years, environmental friendly reagents such as phosphate [9,10], molybdate [11,12], and rare earth metal [13-15] were used for conversion coating treatment. Among which, the phosphate was the most widely used coating treatment, and which was named phosphating treatment. The phosphating treatment could improve the metal's anti-rust ability and the coating performance [16-19]. The phosphate crystals generated during the phosphating treatment could adhere to the surface of the EG steel to form a porous structure which was the weak link of anti-corrosion. Generally, in order to improve the corrosion resistance of the phosphate layer, the phosphated samples need to be treated further with silicate or molybdate for sealing the pores as complete as possible [12,20,21].

In this work, the EG steel was treated by the process of phosphating and sealing treatment which are environmental friendly. A series of measures, for example, adding Mn^{2+}, Ni^{2+} to the phosphating solution and using sodium silicate to seal zinc phosphate coating have been taken to further improve the corrosion resistance of the EG steel [19,22,23]. The electrochemical technique [3,11,12,14,21,24-28], scanning electron microscopy and the neutral salt spray test were used in evaluating the corrosion resistance of the modified samples. By comparing the data of the different kinds of samples directly, we can found that the corrosion resistance of the EG steel was improved significantly by phosphating and sealing treatment.

2. EXPERIMENTAL

2.1 Materials and sample preparation

Three types of samples (50 mm×50 mm) were used in this work: the electro-galvanized (EG) steel, the phosphated electrogalvanized steel (EG+P), the phosphated electrogalvanized steel with post-sealing treatment (EG+P+S). The material used in this study was EG steel with 30 g/m^2 zinc layer produced by industrial production lines (Baosteel Co., Ltd.). After the alkaline degreasing, the EG steel was rinsed with deionized water and dried. The EG steel was immersed in phosphating solution at 55 °C for 90s. After immersion, the samples were rinsed and dried. So the phosphated electrogalvanized steel (EG+P) was obtained. To obtain the samples of EG+P+S, the EG+P samples were sealed with post-sealing solution by immersion at 80 °C for 10 min then rinsed and dried [19,26]. The solutions with the composition and process technologies for phosphating and post-sealing are shown in Table 1.

Table 1. Formulations and process parameters for electro-galvanized steel

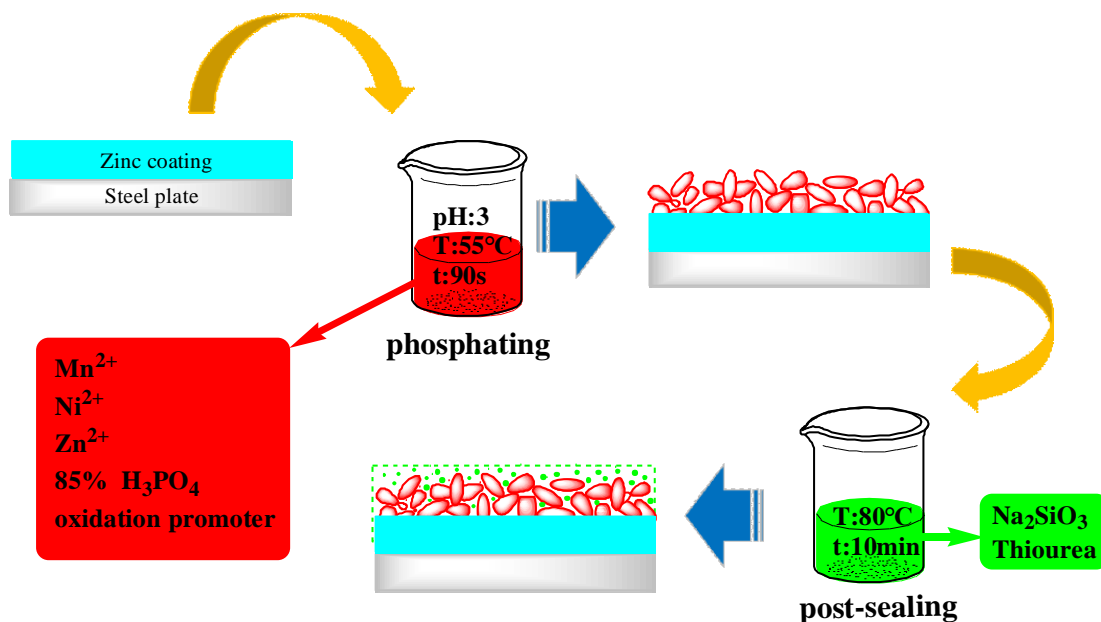|	Formulations	Processes parameter
Phosphating	Mn^{2+}: 0.04 mol/L	pH: 3
	Ni^{2+}: 0.03 mol/L	T: 55 °C
	Zn^{2+}: 0.025 mol/L	t: 90s
	85% H_3PO_4: 11 mol/L	
	oxidation promoter	
Post-sealing	Na_2SiO_3: 8 g/L	T: 80 °C
	Thiourea: 2 g/L	t: 10 min

Figure 1. Schematic diagram of the phosphating and post-sealing for electro-galvanized steel.

2.2 Characterization

The microscopic morphology and element composition of the surfaces were observed by scanning electron microscopy (SEM, Ultra Plus, Carl Zeiss AG, Germany), equipped with energy dispersive spectromter (EDS). All electrochemical measurements were accomplished at room temperature by an electrochemical workstation (CHI660E) with three-electrode arrangement in 5 wt% NaCl solution. The test area was 1 cm². The potentiodynamic polarization test was scanned at a rate of 1 mV/s from –300 mV (relative to the OCP) to +300 mV (relative to the OCP). The electrochemical impedance spectroscopy (EIS) test was obtained with 10 mV as the sinusoidal perturbation in a frequency range between 100 kHz to 0.01 Hz. The ZView2 software was used to simulate the electric elements of the EIS results. Furthermore, the corrosion resistance of the samples was evaluated by a neutral salt spray test. The test was carried out with spraying using 5 wt% NaCl solution (pH: 6.5-7.0), and the temperature of the saturated vapor pressure was 47 °C, the temperature of the sample chamber was 35 °C. The sample was at an angle of 30° to the vertical.

3. RESULTS AND DISCUSSION

3.1 Surface morphology and element composition

Figure 2(a-c) shows the surface morphology of samples. The element composition of different samples corresponding to Figure 2 is listed in Table 2. It can be obviously seen the layer stacking structure on the EG steel surface in Figure 2(a). EG steel surface contains only two elements, Zn and a small amount of O. After the phosphating treatment, the phosphate crystals with the shape of needle and platelets were fine and dense, uniformly covering the surface of the samples with pores as shown in Figure 2(b). EDS results (Table 2) showed that P and a small amount of Mn and Ni appear on the surface of the EG+P. When the EG+P samples were post-sealed with sodium silicate, the edges and corners of the zinc phosphate crystal become blurred. The pores among the crystals are sealed with the film containing Si, P, Zn, Mn, Ni and O, forming a continuous composite coatings on the surface of the EG steel.
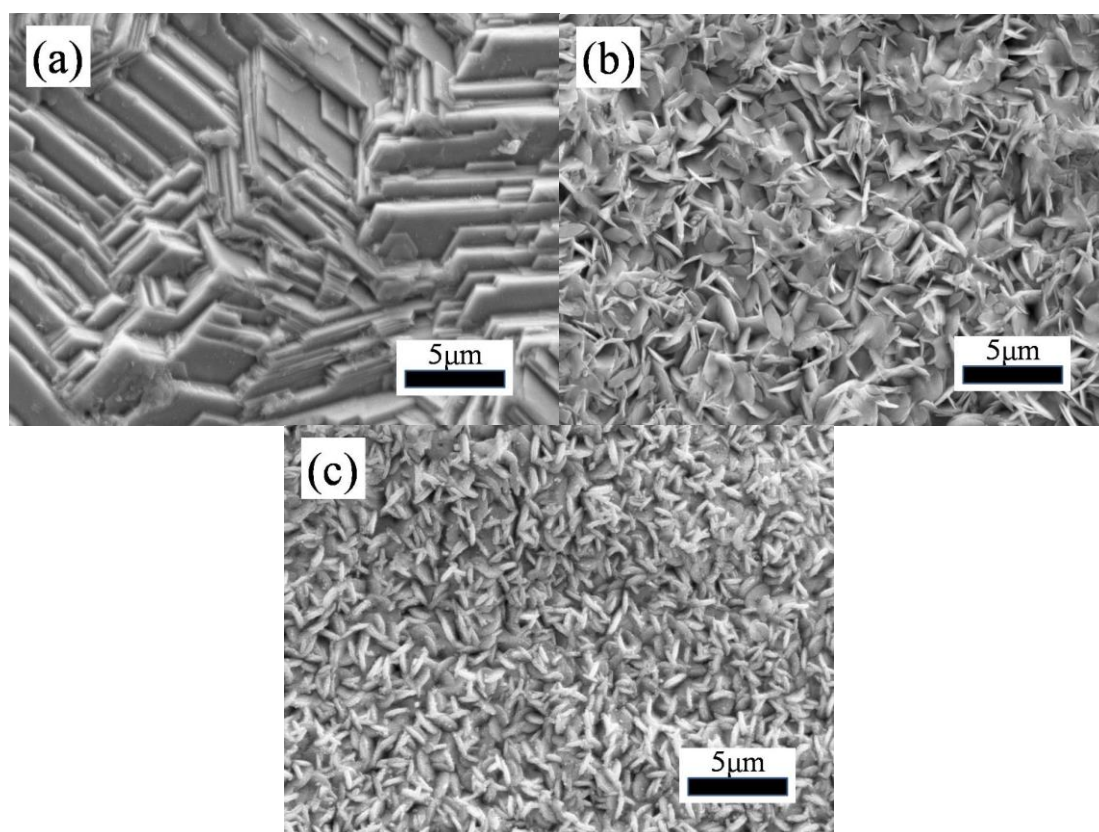

Figure 2. SEM images of (a) EG, (b) EG+P and (c) EG+P+S.

Table 2. The surface element composition of samples (wt%)

	Zn	O	P	Ni	Mn	Si
EG	96.36	3.64				
EG+P	70.01	17.31	9.84	0.53	2.31	
EG+P+S	68.65	19.43	6.25	0.62	2.19	2.86

3.2 Preliminary corrosion tests

Figure 3 shows the corrosion percentage of samples varies with the salt spray time in the salt spray test. It can be found that the corrosion rate of the EG steel is the fastest, and the corrosion area reached 100% only 40h, so the corrosion resistance is obviously bad. The salt spray time of EG+P was significantly extended, which indicated that zinc phosphate crystals exhibit good protection for the EG steel, consequently, the corrosion resistance of EG steel have been extremely enhanced. The corrosion resistance of the samples sealed with sodium silicate was enhanced obviously when compared to the other two samples. After 56h neutral salt spray test, the corrosion percentage of the sample was only 10%. This is mainly because of film contain Si which forming on the phosphate crystal layer during the processing of sealing treatment have further improved the corrosion resistance of the EG steel.
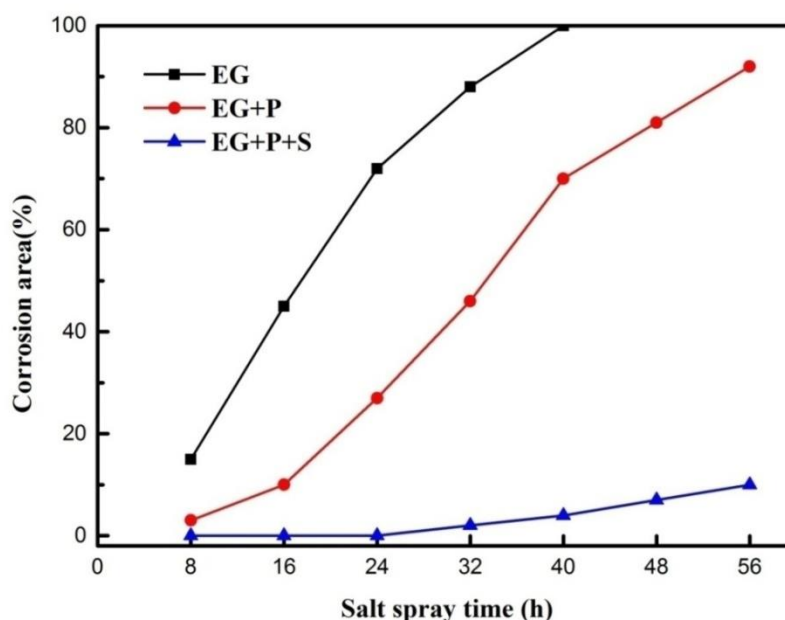

Figure 3. Corrosion area of samples with increasing salt spray time.

3.3 Electrochemical corrosion behavior

Figure 4 presents the potentiodynamic polarization curves of samples in 5 wt% NaCl solution. The corrosion potential and current density determined by extrapolating the anodic and cathodic polarization curves, anodic Tafel slope and cathodic Tafel slope are listed in Table 3. From the trend of the polarization curves of the three samples, we can found that the corrosion rate of the samples in 5 wt% NaCl solution was controlled by the cathodic reduction process. After phosphating treatment, anodic Tafel slope decreases significantly, while cathodic Tafel slope increases. We can find the corrosion current density of coating decreased by an order of magnitude (from 1.390×10^{-5} A·cm^{-2} to 1.980×10^{-6} A·cm^{-2}). Meanwhile, the corrosion potential gradually shifted to a higher potential (from -1.112V to -1.059V). The phenomenon shows phosphate on the surface of the EG steel reduces the active sites on the zinc surface by covering. Phosphate coating has good barrier effect on the

permeation of Cl⁻ in the solution. Post-sealing the phosphated EG steel with sodium silicate solution, the trend of changes in Tafel slope was consistent with the phosphated EG steel. The corrosion current density decreased to 1.559×10^{-6} A·cm^{-2}, further, corrosion potential shifted to -1.029V. The right shift of the anodic and cathodic branches for EG+P+S is great. After post-sealing treatment, the Si-containing film formed on the surface fills the pores of the phosphate coating and covers the active area of the zinc surface [12,21,22,24,29]. It was suggested that the anodic and cathodic processes of zinc corrosion are suppressed effectively by the complete silicate films. When the EG steel was phosphated and post-sealed, the anodic oxidation and the cathodic reduction reaction of zinc were suppressed so that the anodic polarization curve and the cathodic polarization curve move in a direction to which the current decreases, effectively reducing the active dissolution of zinc, indicating that the EG steel has good corrosion resistance.

The corrosion protection efficiency, Pe (%) is used to indicate the ability of the coating to protect the substrate. Pe (%) of the samples was calculated by the following expression [12,21]:

$$Pe(\%) = (1 - i_{corr}/i_{corr}^0) \times 100 \qquad (1)$$

Where i_{corr} and i_{corr}^0 were the corrosion current densities of the samples and the substrate. The corrosion current density of the substrate was 6.212×10^{-5} A·cm^{-2}. The corrosion protection efficiency of samples are shown in Table 3. The Pe value of the EG steel was 77.7 %, while the Pe values of samples were higher than 99% after the phosphating and post-sealing treatment, so the phosphating and post-sealing treatment for the protection to the substrate was significantly higher than the EG steel. In other words, phosphating and post-sealing treatment on the EG steel played a good protective effect, improving greatly the corrosion resistance of EG steel.
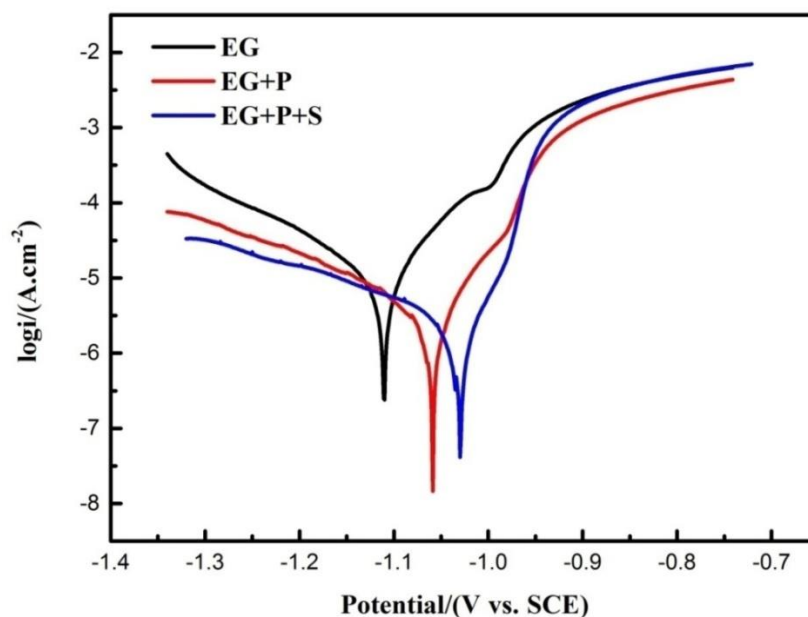

Figure 4. Potentiodynamic polarization curves of samples in 5 wt% NaCl solution.

Table 3. Electrochemical parameter by potentiodynamic polarization

Samples	E_{corr}/V	I_{corr}/A·cm^{-2}	β_a/V·dec^{-1}	β_c/V·dec^{-1}	Pe(%)
EG	−1.112	1.390×10^{-5}	0.124	0.137	77.7
EG+P	−1.059	1.980×10^{-6}	0.038	0.172	99.7
EG+P+S	−1.029	1.559×10^{-6}	0.044	0.228	99.8

Figure 5 shows Nyquist plot of samples in 5 wt% NaCl solution. The shape of the Nyquist plot for samples is identical: one capacitive loop in high frequency region; one capacitive loop and one inductive loop in low frequency region. In general, for EG steel, the inductive loop in high frequency region is due to the hindering effect of the corrosion products to the electrons transfer. EG steel was easy to produce corrosive pores resulting from the thin zinc layer. Low frequency capacitive loop can be attributed to the diffusion of electrolyte between the pores of the corrosion product formed by zinc or the pores of the zinc layer. The inductive loop in low frequency region is representative of the dissolution of zinc [21,30,31]. To the phosphated EG steel (EG+P), high frequency capacitive loop is related to the effect of the silicate coating. In the case of the sample of EG+P+S, high frequency capacitive loop is due to phosphate coatings and silicate films. For these two samples (EG+P) and (EG+P+S), the low-frequency capacitance loop can be attributed to the diffusion of the electrolyte between the pores of the protective coating [21,24,32]. The inductive loop in low frequency region can be attributed to the dissolution of zinc. In comparison with the electrochemical impedance values of the EG steel, the values of the samples with phosphating treatment and post-sealing treatment were significantly increased. The value of phosphating treatment was about 5 times than that of EG steel. Phosphate treatment forms a layer of phosphate on the surface of the EG steel covering the zinc layer, which played an inhibitable role in the corrosion process. The impedance values of the EG+P+S were increased by an order of magnitude than that of the EG steel. The silicate coating on the phosphate formed by the post-sealing treatment has a very good protective effect on the zinc and improves the corrosion resistance greatly.
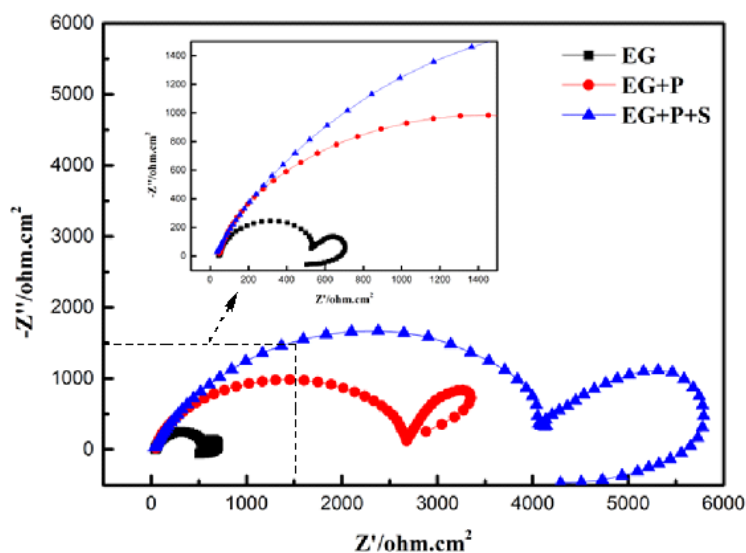

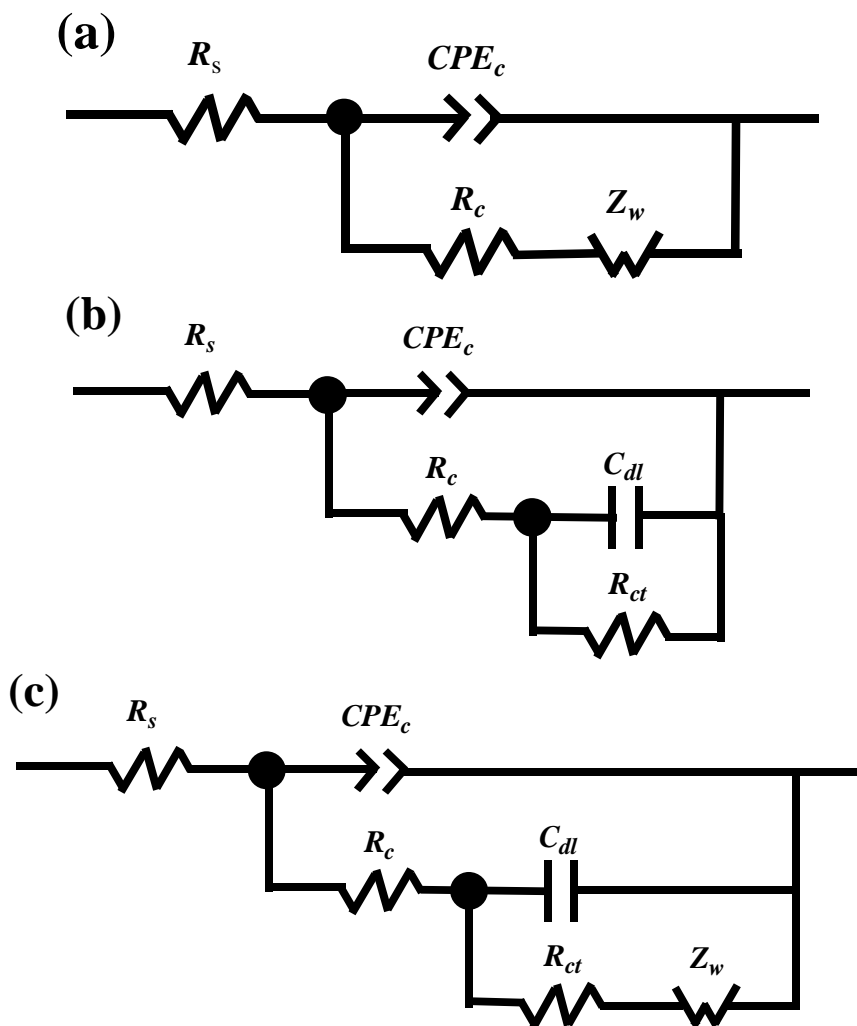**Figure 5.** Nyquist plots of samples in 5 wt% NaCl solution

Figure 6. Equivalent circuit of (a) EG steel, (b) EG+P and (c) EG+P+S, in 5 wt% NaCl solution.

Table 4. Equivalent Circuit Fitting Parameters of sample

Samples	R_c (Ω cm^2)	CPE_C (Ω^{-1} cm^{-2} s^n)	R_{ct} (Ω cm^2)	C_{dl} (F cm^{-2})
EG	4.66×10^2	5.64×10^{-6}		
EG+P	2.63×10^3	1.40×10^{-6}	1.05×10^3	2.31×10^{-3}
EG+P+S	4.37×10^3	1.37×10^{-6}	1.14×10^3	2.59×10^{-4}

Figure6 (a-c) shows the equivalent circuit to simulate the EIS data without the inductive loop, respectively. Table 4 summarizes the values of the electric elements simulated using the ZView2 software. R_s represents the solution resistance between the working electrode and the reference electrode resulting from the ohmic or uncompensated resistance of the solution. R_c is the layer resistance related to the structure of the chromate layer, which is in parallel with CPE_C, coating resistance [21,24]. R_{ct}, the charge transfer resistance, is in parallel with C_{dl} which represents the double layer capacitance [29]. The phosphating treatment increased the Rc value about 5 times than that of the EG steel, after post-sealing that becomes 10 times. For coating, the greater the value of Rc is, the better

the protection of metal substrate is, which indicates that the phosphating and post-sealing treatment increased the protection on the EG steel [22], and increased the corrosion resistance. The charge transfer resistance (R_{ct}) of the coating characterizes the ease of electrode reaction. The R_{ct} value of the three samples increased gradually. Fewer active areas on the phosphate conversion coating result in a higher charge transfer resistance. The post-sealing process fills the pores of the phosphate and forms a complete silicate film on the surface overcoming the disadvantages of phosphate coatings with pore, further inhibiting the corrosion reaction.

4. CONCLUSION

In summary, the active zinc region of the electro-galvanized (EG) steel was covered by the porous phosphate layer generated during the process of phosphating treatment, and which could inhibit the corrosion process obviously. The phosphate pores were filled and covered with membrane layers containing Si after post-sealing treatment with sodium silicate, and a layer of completely silicate film was formed, therefore, the corrosion protection efficiency of the electro-galvanized steel was significantly improved after the phosphating and post-sealing treatment. The corrosion area of the EG steel modified by phosphate and sodium silicate was controlled under 10% after a 56 h of salt spray test. The electrochemical tests confirm phosphating and post-sealing treatment reduce the corrosion current density of the electro-galvanized steel by an order of magnitude and make the corrosion potential shift to a higher potential. Furthermore, the electrochemical impedance values of the sealed samples were increased by an order of magnitude than that of the electro-galvanized steel. Phosphating and post-sealing treatment inhibit the corrosion of zinc anode and cathode process, so the corrosion resistance of EG steel is greatly improved. The method is simple and effective, and presents potential applications in industries.

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