Int. J. Electrochem. Sci., 11 **(2016)** 2306 - 2316

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Performance Improvement of Phosphate Coating on Carbon Steel by Cathodic Electrochemical Method

Shuo-Jen Lee, Do Le Hung Toan[*], *Yi-Ho Chen, Huan-Chih Peng*

Department of Mechanical Engineering, Yuan Ze University, Taoyuan, Taiwan, R.O.C.
[*]E-mail: toandlh@gmail.com; s1028705@mail.yzu.edu.tw

Received: 22 December 2015 / *Accepted:* 19 January 2016 / *Published:* 1 February 2016

Phosphate coatings are formed in order to protect the surfaces of low carbon steel from corrosion. The coatings formed by immersion and cathodic electrochemical methods are compared based on their weight, porosity, surface composition and anti-corrosion performance. In this study, coating mass is determined by a gravimetric method. The porosity of the phosphate coatings was examined by using the polarization electrochemical test. The anti-corrosion performance of the coatings was evaluated by salt spray test, and electrochemical characterization which was performed in 3.5% NaCl solution at 25ºC. The surface morphology and chemical composition of phosphate coatings were investigated *via* scanning electron microscopy accompanied by energy-dispersive X-ray. The findings showed that cathodic electrochemical method has advantages over conventional coatings in terms of coating thickness, porosity, and anti-corrosion performance.

Keywords: Phosphate coating, electrochemical method, carbon steel.

1. INTRODUCTION

Phosphate coating, which is the most common metal pretreatment process for ferrous and non-ferrous metal, protects metal surfaces by creating a protective film [1-4]. This is not only an economic process due to high speed of operation, but also adaptable to production requirements for articles of all sizes, and for large or small number of products [5, 6].

After a dilute solution of phosphoric acid and phosphate salts is applied *via* spraying or immersion, the phosphate chemically reacts with the metal surface to form a layer of insoluble, crystalline phosphates such as Fe, Mn, Zn or mixtures of phosphate salts. The selected phosphate coating depends on the application. For example, to provide high wear resistance and corrosion protection, the phosphate coating must be uniform, finely structured, and firmly adhered to the metal surface. Phosphate film can be an effective and inexpensive base for a painted surface. The protection provided by a phosphate film depends on the phosphate salt concentration in the solution the process time, surface components, and state of the surface before placement.

Normally, in order to create an effective coating, phosphating processes are conducted at relatively high operating temperatures ranging from 60 to 95ºC with longer coating time, thus high energy input is needed [7]. Many methods have been used such as changing surface treatment methods, accelerators, or the composition of the phosphating solution to lower the temperature in order to save energy [8-11].

Applying phosphate coatings by electrochemical method has several advantages over conventional phosphate coating methods. Electrochemical phosphating is a simple process that provides good coating quality at a low production cost. However, few recent studies have discussed electrochemical phosphating [12-14]. This study found that electrochemical phosphating can considerably enhance coating quality. In this study, cathodic electrochemical phosphating is evaluated and adopted to phosphating in order to form high-quality phosphate coatings.

2. EXPERIMENTAL

2.1 Sample preparation

Table 1 shows the compositions of the low-carbon steel substrates used for the deposition of coatings by phosphating process, which had dimensions of 5cm x 3cm x 0.4cm. The pre-treatment process is performed in a series of five stages. The first stage is degreasing, in which the surface is cleaned to remove contaminants such as oils, greases and corrosion products. In the following polishing stage, the samples are mechanically polished with sandpaper. In the third stage, samples are immersed in alkaline solution for 5 minutes. Next, the samples are immersed for 10 minutes in hot water and then for 10 minutes in cold water. Finally, in the drying stage, samples are dried with compressor air.

Table 1. Chemical compositions of steel substrate used for phosphate coating experiments

Element	C	Mn	P	Ni	Mo	Fe
Composition (wt. %)	0.12	0.42	0.002	0.094	0.012	balance

2.2. Phosphate coating fabrication

The phosphating solution were prepared from 60 g/L $Zn(NO_3)_2.6H_2O$, 35 g/L $Mn(H_2PO_4)_2.2H_2O$, additives and distilled water. Table 2 shows the operating conditions for the phosphating bath and characteristics of this solution. The bath parameters, including free acidity (FA) and total acidity (TA) of the solution, were determined by titration of the solution with standard 1.0 N NaOH. Phenolphthalein or methyl orange was used as the indicator [14].

Samples in this study were phosphated using two different type of process conditions, methods of immersion and cathodic electrochemical. With the immersion method, steel samples after surface treatment were only immersed in a phosphate solution for 10 minutes at 70ºC. In the cathodic electrochemical method, a steel sample formed the working electrode at the cathode, which was placed between two large stainless steel counter electrodes. The cathodic electrochemical phosphating process were performed at a constant current density (10 mA/cm^2) using a DC power supply system and carried out at 70ºC. The processing time was set at 10 minutes. The samples after fabricated by immersion and cathodic electrochemical methods were then rinsed with deionized water to remove the soluble salts and acid residues. Afterward, all of samples were dried using compressed air. Finally, the samples were stabilized in a desiccator for 24 hours before testing the coating properties.

Table 2. Operating conditions of phosphating bath and characteristics of phosphating solution

Parameters	Conditions and Characteristics
Total Acid value (points)	60
Free Acid value (points)	6
pH	2.2
Temperature (ºC)	70 ± 2 ºC
Current density (cathodic electrochemical method)	10 mA/cm^2

2.3. Determining coating weight

The mass of the phosphate coating and the dissolved mass of the metal substrate are important factors widely use in industries to evaluate the quality of phosphate coating [12]. In this study, a gravimetric method was used to measure coating weight [14]. An analytical scale is used to weigh the substrates before and after phosphating. The procedure for measuring coating weight was as follows. After phosphating, coatings are dissolved by immersion in a solution containing Na_4ETDA 12%; NaOH 9%; TEA 4% and H_2O 75% at 70ºC for 10 minutes. Next, substrates are rinsed dried at 70ºC, and then weighed again with an analytical balance. The phosphate coating mass per unit surface area (M_1) was estimated by equation 1:

$$M_1 = \frac{m_2 - m_3}{S}, g/m^2 \qquad \text{(eq.1)}$$

The dissolved mass of the metal substrate per unit surface area (M_2) has been calculated according to the equation 2:

$$M_2 = \frac{m_1 - m_3}{S}, g/m^2 \qquad \text{(eq.2)}$$

where: m_1 - original weight of specimen (g); m_2 - weight of specimen after phosphating (g); m_3 - weight of specimen after removing the coating film (g); and S - sample surface area (m^2).

2.4. Porosity estimation

The porosity of phosphated steel can be determined by comparing currents measured for a coated sample and a bare steel sample of the same overall area, provided that the oxygen reduction reaction is kinetically controlled and anodic reactions are negligible [15]. The electrolyte used in this study was a 35.5 g/L Na_2SO_4 solution at 25ºC. Before performing the electrochemical test, the electrolyte was aerated by stirring for 10 minutes. Polarization was performed under an open circuit corrosion potential varying from -2.0V to 0V at a scan rate of 5 mV/s. Polarization measurements were performed with a Solartron 1285 Potentiostat, with Solartron Corrware and Corrview software for data acquisition and plotting. The porosity was calculated according to the following formula:

$$P = \frac{I_{ACF}}{I_{ASF}} \times 100\% \qquad \text{(eq.4)}$$

where: P – porosity of phosphate coating (%); I_{ACF} - the average current density for phosphated steel (A/cm^2); I_{ASF} - the average current density for steel without phosphate coating (A/cm^2).

2.5. Evaluating anti-corrosion performance

In order to estimate the anti-corrosion performance impacted by the phosphate coatings, the phosphate coated samples were subjected to a salt spray test and electrochemical characterization [16]. A salt spray test was performed for 24 hours according to the ASTM B117 standard. The apparatus required for salt spray exposure consists of a fog chamber and a salt solution prepared by dissolving 5 ±1 parts by mass of sodium chloride (NaCl) in 95 parts of water. For this test, the solution collected after atomization at 35°C should have a pH ranging from 6.5 to 7.2. Polarization was performed from the open circuit corrosion potential from -2.0 V to 0.5 V with a scan rate of 0.5 mV/s. The electrolyte is 3.5% NaCl solution. The test is performed at room temperature (25ºC). The polarization measurements are made using a Solartron 1285 Potentiostat, with Solartron Corrware and Corrview software for data acquisition and plotting. The electrochemical measurements were conducted using a conventional three-electrode electrochemical cell with the bare or coated sample as a working electrode, a platinum plate as auxiliary electrode and a saturated calomel electrode (SCE) as the reference.

2.6. Surface morphology and chemical composition analysis

Surface morphology of the phosphate coating was captured *via* scanning electron microscopy (SEM). Energy-dispersive X-ray spectroscopy (EDX) is used to detect elements on sample surfaces [9, 14 and 16]. Samples coated with phosphating solution were cut into 0.5×0.5 cm^2 squares for scanning electron microscope (SEM) studies. The images were captured at a magnification of 500× and a quality elemental identification of some of the crystals seen in the phosphate coat was performed using the SEM-EDX combination.

3. RESULTS AND DISCUSSION

3.1. Mass of phosphate coating and dissolved mass of metal substrate in phosphating process

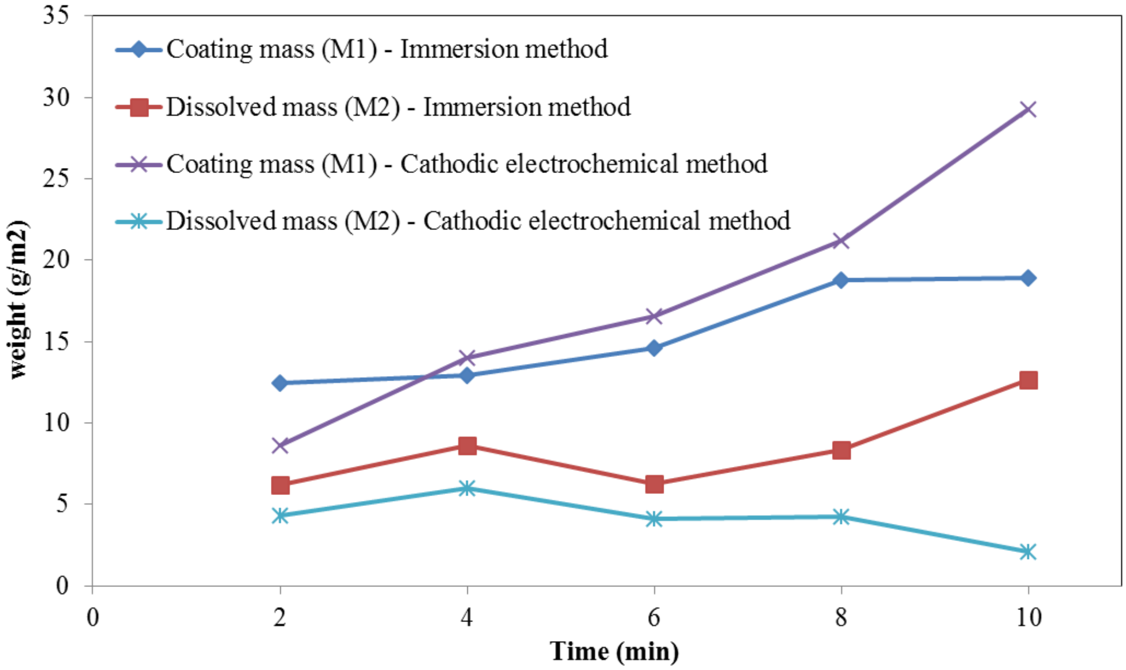

Figure 1. Variation of the phosphate coating mass per unit surface area (M_1) and the dissolved mass of the metallic substrate per unit surface area (M_2) of coatings fabricated by immersion method and cathodic electrochemical method at various phosphating time

The mass of the phosphate coating and the dissolved mass of the metal substrate are important factors in the phosphating process. Figure 1 presents the results of the phosphating process. The experiments show that the mass of the phosphated coatings increase as the deposition time of the phosphating process increases. The experiments show that the phosphate coating mass (M_1) of coatings formed by immersion method increases with time until the period between eighth to tenth minutes. The mass then plateaus at 19 g/m^2. Phosphating process starts with the acidic solution etching the overlying oxide to allow the metal to come in contact with the solution. The process in this stage, which is called induction, does not form a phosphate coating on the surface. During the induction stage, the oxide film remains on the surface even after cleaning. In the second stage, the first nuclei are formed, and the nucleation rate increases rapidly with time. In the main exponential growth stage, coating mass increases with the precipitation of zinc phosphate coating. The coating mass per unit surface area (M_1) and the dissolved mass of metallic substrate per unit surface area (M_2) increase simultaneously with phosphating time. As the surface becomes completely precipitated, the rate of increases in the weight of the phosphate coating slows and then stops. The phosphate coatings have a high density and no cracks or gaps. These reasons explain why the phosphate coating mass per unit surface area (M_1) reaches at a stable status (about 19 g/m^2). The dissolved mass of metal substrate per unit surface area (M_2) also increases with time and reaches a maximum at 12 g/m^2.

During the cathodic electrochemical phosphating processes, the phosphate coating mass per unit surface area (M_1) increases with time. The metal substrate used as the cathode was forced to deposit due to the applied current. The hydrogen evolution reaction occurred at work-piece lead to the raise in interfacial pH in the electrolyte [14]. This helps the soluble primary phosphate converted into insoluble tertiary phosphate and deposited onto the low carbon steel substrate. During this process, zinc is deposited on the carbon steel substrate and iron dissolution is also limited because the work-piece is forced to deposit under DC conditions. This evidences that the dissolution of metallic substrate per unit surface area (M_2) during the phosphating processes is very low (approximately 2 g/m^2 after 10 minutes phosphating).

Comparing the mass of phosphate coating obtained by immersion and cathodic electrochemical methods reveals that the cathodic electrochemical method can produce good quality coatings and can form coatings of the desired thickness. Cathodic electrochemical phosphating can form a heavy surface coating (heavier than 30 g/cm^2). The reported of Jegannathan et al. [12] also indicated that the electrical parameters in electrochemical phosphate coating process support building of a desired coating thickness. Moreover, the mass of iron-dissolute produced by cathodic electrochemical method is very small. There is no ferric phosphate sludge formation in the phosphating solution. Hence, phosphate coating by cathodic electrochemical method can be classified as an eco-friendly process. Therefore, samples after phosphated by cathodic electrochemical method, even unpainted, have high corrosion-resistant performance.

3.2. Porosity of phosphate coating

Table 3. Porosity of phosphating film with different conditions

Method	Average of current density (A/cm^2)	Potential range (Voltage)	Porosity (%)
Without phosphate	4.67×10^{-3}	-	-
Coating fabricated by immersion method	3.32×10^{-3}	-1.8 to -1.4	71
Coating fabricated by cathodic electrochemical method	9.75×10^{-10}	-1.8 to -1.4	dense

Estimation of the porosity of the phosphate coating in this study involves an electrochemical method. The porosity of coatings equals the ratio of current density values at an area where the reduction of oxygen preferentially occurs in the polarization curves. Table 3 shows the porosities of the phosphate samples. The coating obtained by immersion method has a current density of 3.32×10^{-3}A/cm^2. This current density is lower than that of coating obtained for the low carbon steel surface without a phosphate layer (at $4.67\text{x}10^{-3}$ A/cm^2). The coating formed by immersion method is quite coarse and shows a high porosity of 71%. This results is in accordance with the results of Lins et al. [15] which were obtain using electrochemical technique of voltammetric cathodic polarization. Coating fabricated by cathodic electrochemical method obtains a very compact phosphate coating with a porosity equivalent of 0%. This result demonstrates that the coatings formed by cathodic electrochemical method are very dense and good for corrosion protection.

Comparisons of the immersion and cathodic electrochemical methods shows that the latter produced less porous phosphate coatings. The anti-corrosion performance of carbon steel is affected by the porosity of phosphate coatings. As porosity decreases, anti-corrosion performance increases.

3.3. Anti-corrosion performance of phosphate coating:

The anti-corrosion performance of phosphate coatings was evaluated using a salt spray test and an electrochemical characterization. In the salt spray test, samples with and without phosphate coatings were placed in the chamber for 24 hours. By visual observation from Figures 2(a), the low carbon steel substrate which was phosphated by immersion method had red rust after 24 hours of salt spray test and showed inferior anti-corrosion performances. The samples phosphated by cathodic electrochemical method, in which only few red rust appear on the surface of coating, have considerably better anti-corrosion performances. The absences of red rust indicate that the coatings are uniform and dense. As can be seen from Figure 2 (b), the formation of zinc based corrosion product appears on the surface of phosphate coating after cathodic electrochemical phosphating process. This can be explained by the sacrificial effect and deposits of zinc on the surface, that improving the corrosion resistance of coating [13].

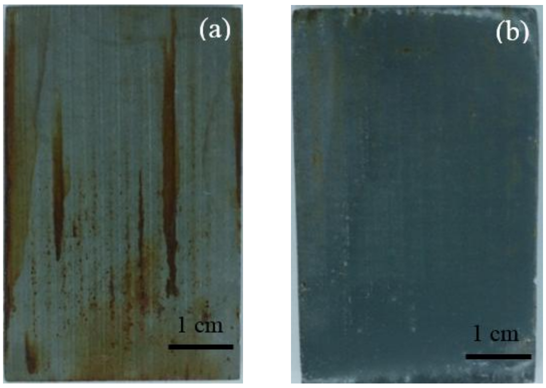

Figure 2. Appearances of samples phosphated by (a) immersion method and by (b) cathodic electrochemical method after 24-hour salt spray test

As can be seen from the polarization curves of phosphate coating (Figure 3), both immersion and cathodic electrochemical methods when compared with un-coated samples showed a linear behavior of potential (E) versus current density (I). Table 4 lists the corrosion potentials and corrosion current densities obtained from the polarization curves. With observation from polarization curves, we can see that cathodic electrochemical method helps to improve the anti-corrosion performance of phosphate coating. These results correlate with those observed in the salt spray test. The experiments showed that the corrosion current density decreased from 1.19×10^{-4} A/cm^2 of the bare steel to 4.77×10^{-10} A/cm^2 of the phosphated samples using cathodic electrochemical method. Additionally, the corrosion potential of phosphate substrates, which were phosphated by immersion and cathodic electrochemical methods, shifted to a nobler direction, which indicated that the phosphate layer markedly improved the corrosion resistance of steel substrate. Hence, the coatings formed by immersion and cathodic electrochemical methods had lower corrosion rates and higher corrosion resistance compared to the raw low carbon steel substrate. Polarization measurement in 3.5% NaCl solution showed that the use of cathodic electrochemical method of the phosphating caused an enhancement in the corrosion resistance of phosphated samples.

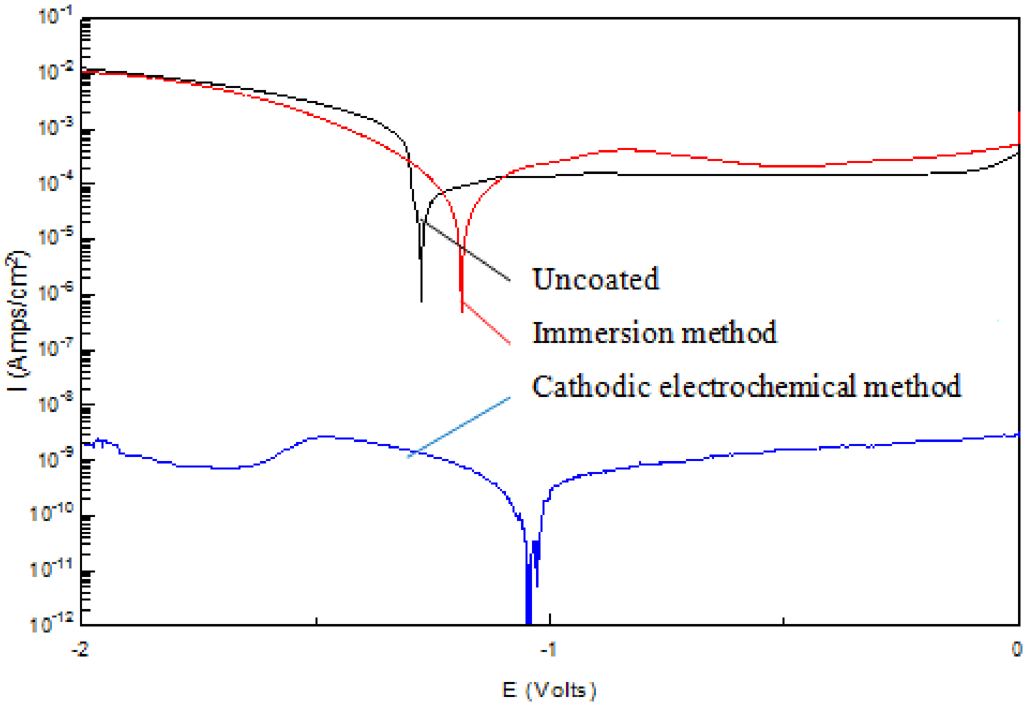

Figure 3. Polarization curves for phosphate coatings obtained by immersion method and by cathodic electrochemical method in comparison with un-coated samples

Table 4. Corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of phosphate coatings

Method	E_{corr} (Volts)	i_{corr} (A/cm^2)
Without phosphated	-1.28	1.19×10^{-4}
Coating fabricated by immersion method	-1.18	8.00×10^{-5}
Coating fabricated by cathodic electrochemical method	-1.04	4.77×10^{-10}

3.4. Surface morphology and chemical composition:

Figures 4 (a) and (b) show scanning electron micrographs of the phosphate coatings formed by immersion and cathodic electrochemical methods, respectively. It is observed that, the surface morphology of coatings obtained by immersion and cathodic electrochemical methods exhibits the formation of flower-like crystals (Figure 4(a)). However, the phosphate coatings obtained by the cathodic electrochemical method are rich in hopeite phase which has formation of plate-or-flower-like crystals (Figure 4(b)). Moreover, the morphology of coating obtained by the cathodic electrochemical method resembles that of the electrodeposited zinc coating [17].

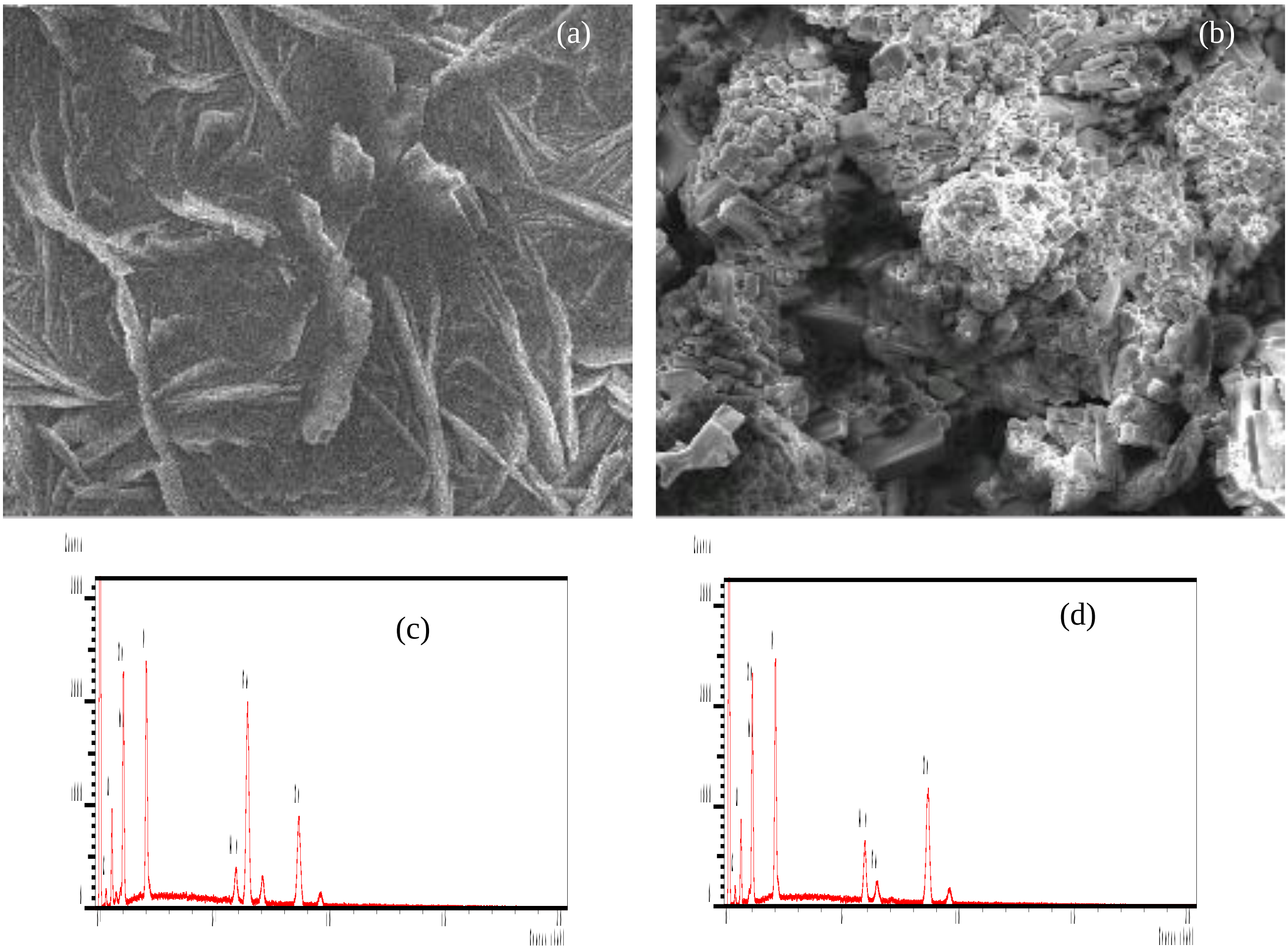

Figure 4. (a) SE micrographs of phosphate coatings formed by immersion method; (b) SE micrographs of the phosphate coatings formed by cathodic electrochemical method; (c) EDX analysis of phosphate crystal formed on carbon steel surface by immersion method; (d) EDX analysis of phosphate crystal formed on carbon steel surface by cathodic electrochemical method

Energy-dispersive X-ray spectroscopy (EDX) technique is used to analyse elements on the sample surfaces. Figure 5 shows the results of EDX analysis of chemical compositions of the phosphate coatings. The phosphate coatings mainly contain manganese, zinc, iron and phosphorus. The composition of the surface coating depends on the substrate and on the process conditions. When the immersion method was used in the phosphating processes, the amount of iron in the coatings, which is the main factor in resistance to surface rusting, approximates 15%. However, the amount of iron on the coating formed by cathodic electrochemical method is only 2%. This indicates that cathodic electrochemical phosphating obtains surfaces with a low amount of iron. This means that the coating has low possibility to form red rust because of the less iron and low porosity. Moreover, the percentage of zinc in the coatings also increases when using cathodic electrochemical method. The amount of zinc is higher than 24% when we conduct the phosphating processes by cathodic electrochemical method. This phenomenon can be explained by the zinc deposition during the phosphating processes. A special feature of cathodic electrochemical method is the formation of zinc – zinc phosphate coating which acts as a barrier protect steel substrate against corrosive environment [18]. The ratio of Zn/Fe increases when we apply cathodic electrochemical phosphating. This result indicates that the risk to get rust on the coating considerably decreases.

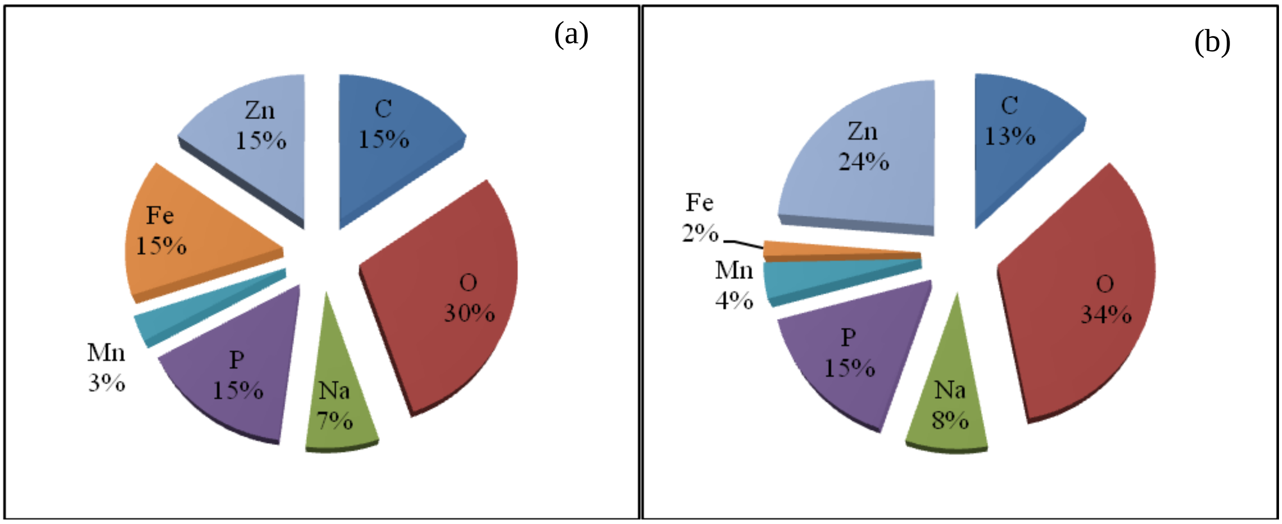

Figure 5. Chemical composition of phosphate coating formed by (a) immersion method and by (b) cathodic electrochemical method.

4. CONCLUSIONS

The cathodic electrochemical method shows many advantages on the phosphate coating process. This study compared coatings obtained by different phosphating processes in terms of the mass of the phosphate coating, the dissolved mass of the metal substrate, the porosity of the phosphate coating, the surface composition, and anti-corrosion performance. With cathodic electrochemical method, coating mass is higher than that obtained by immersion method. This result indicates that cathodic electrochemical method can produce good quality coatings and can form coatings of the desired thickness. The dissolved mass of metal substrate in cathodic electrochemical phosphating process is very low lead to no ferric phosphate sludge formation in phosphating bath. Hence, phosphate coating by cathodic electrochemical method can be classified as an eco-friendly process. The results of salt spray test are consistent with the results observed by polarization measurement, and indicating that the use of cathodic electrochemical method on phosphating process enhanced the corrosion resistance of phosphate coating. This due to a very low porosity phosphate layer and the formation of zinc – zinc phosphate coating fabricated by cathodic electrochemical method acts as a barrier protect steel substrate against corrosive environment. Surface composition analysis by energy-dispersive X-ray spectroscopy revealed that cathodic electrochemical phosphating obtains surfaces with high amount of zinc and low iron, which reduces the risk of rust on the coating considerably decreases.

ACKNOWLEDGEMENTS
This work was accomplished with much needed support and the authors would like to thank for the financial support by Ministry of Science and Technology of R.O.C. through the grant MOST 103-2221-E-155-023.

References

1. T. S. N. Sankara Narayanan, *Rev. Adv. Mater. Sci*., 9, (2005) 130
2. G. Lorin, *Phosphating of Metals*, Finishing Publications Ltd., London (1974)
3. W. Rausch, *The Phosphating of Metals*, Finishing Publications Ltd., London (1990)
4. D.B. Freeman, *Phosphating and Metal Pretreatment - A Guide to Modern Processes and Practice*, Industrial Press Inc., New York (1986)
5. P. Pokorny, P. Szelag, M. Novak, L. Mastny, V. Brozek, *Metalurgija*, 54 (2015) 489
6. Q. Y. Xiong, Y. Zhou, J.P. Xiong, *International Journal of Electrochemical Science*, 10 (2015) 8454
7. S. Shanmugam; K. Ravichandran; T. S. N. Sankara Narayanan; M. Marappan, *Corrosion Engineering Science and Technology*, 49 (2014) 719
8. K. Abdalla, A. Rahmat and A. Azizan, *Advanced Materials Research*, 626 (2013) 183
9. K. Abdalla, A. Rahmat and A. Azizan, *Advanced Materials Research*, 626 (2013) 569
10. Y. Totik, *Surface and Coatings Technology*, 200 (2006) 2711
11. F. Fang, J.H. Jiang, S.Y. Tan, A.B. Ma, and J.Q. Jiang, *Surface and Coatings Technology*, 204 (2010) 2381
12. S. Jegannathan, T.S.N. Sankara Narayanan, K. Ravichandran and S. Rajeswari, *Surface and Coatings Technology*, 200 (2006) 6014
13. S. Jegannathan, T.S.N. Sankara Narayanan, K. Ravichandran and S. Rajeswari, *Surface and Coatings Technology*, 200 (2006) 4117
14. P.K. Sinha, *Surface and Coatings Technology*, 161 (2002) 158
15. C.H.S.B. Teixeria, E.A. Alvarenga, W.L. Vasconcelos and V.F.C. Lins, *Materials and Corrosion*, 62 (2011) 771
16. M. Manna, *Surface and Coatings Technology*, 203 (2009) 1913
17. C. Cachet, F. Ganne, S. Joiret, G. Maurin, J. Petitjean, V. Vivier and R. Wiart, *Electrochimica Acta*, 47 (2002) 3409
18. S. Jegannathan, T.K. Arumugama,T.S.N. Sankara Narayanan and K. Ravichandran, *Progress in Organic Coatings*, 65 (2009) 229