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# ELECTROCHEMICAL PHOSPHATE CONVERSION COATINGS: A REVIEW

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Deposition of phosphate conversion coating using electrochemical methods have many advantages such as low phosphating temperature, low energy cost and good properties of fabricated coating and in recent times increasingly employed for deposition of phosphate coating. Deposition mechanism of coating which is fabricated using electrochemical methods is different from those obtained by conventional chemical methods, consequently, the properties of electrophosphate coating is also different from those conventional phosphate coating. In this paper, recent understanding of deposition mechanism of electrophosphate coating is reviewed. The microstructure, composition, thickness and corrosion behavior of electrophosphate coatings and effect of different factors of those properties were also reviewed.

*Keywords*: Phosphate conversion coating; electrochemical methods; corrosion behavior; microstructure.

## 1. Introduction

Phosphating is one of the important chemical conversion treatments for pre-treatment on metal surfaces and industrial applications.[1–10] Thus, the phosphate methods have been developed through the invention of new industries.[11–13] These coatings are employed in several industries to increase corrosion resistance, surface preparation for painting and decorative applications.[14–16] These coatings are applied on several metal layers such as steel,[17–20] magnesium,[21–25] galvanized steel,[26–30] and aluminum.[31,32] In general, many phosphate baths are zinc base,[33,34] magnesium base[35–37] and iron base[38,39] and by adding different cations such as nickel cation,[40,41] calcium cation,[42,43] niobium cation,[44] and copper cation, two or three cationic baths will be generated. Many of the reported phosphate baths require high operation temperature, the major problem of this bath is that it requires high amount of energy which is recently one of the crises all over the world. Moreover, utilizing and keeping thermal coils are difficult as a result of deposit formation that leads to overheating of bath and thus the requirement of coil substitution increases. Another problem is overheating of the bath solution that can quickly convert initial phosphate into third phosphate and thus increase the free acidity of the bath and cause the delay in deposition of phosphate coating.[45,46] One way to overcome these difficulties is utilizing low temperature bath, but low

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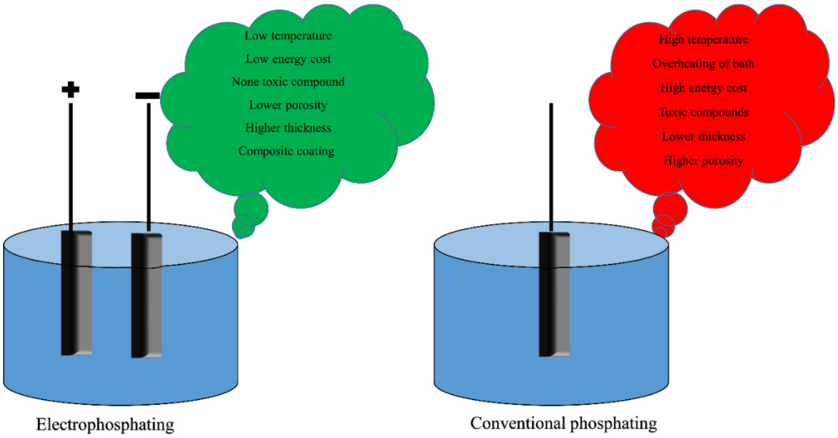


Fig. 1. Compression between conventional chemical phosphating and electrochemical phosphating.

temperature phosphate process is very slow and must find ways to increase coating rate. By employing chemical,[47,48] electrochemical[49–52] and mechanical accelerators,[53] the process rate can be increased, but each of these methods has advantages and disadvantages. In low temperature bath, nitric acids are usually utilized as accelerators, but a lot of nitrate is required to increase the deposition rate of phosphate. Moreover, nitrates are classified as toxic materials, therefore the use of nitrates as accelerators can cause harmful effects on the environment.[54–57] Recent advances have made it possible to use electrochemical methods to carry out phosphate process with the goal of achieving thicker layers of phosphate with better properties at lower temperatures and times.[58] Since the electricity current is acting as accelerator in this process, the chemical accelerators can be removed by applying electricity, so this method has less environmental pollution.[59,60] The comparison between the chemical and electrochemical phosphate is schematically illustrated in Fig. 1. The aim of this article is to review the mechanism and properties of phosphate coatings generated by electrochemical methods, which means the mechanism of the coatings and the resulting properties of these coatings will be reviewed.

## 2. Formation Mechanism of Phosphate Coating via Electrochemical Methods

Generally, electrochemical methods for applying phosphate coatings include cathodic and anodic methods. In cathodic and anodic electrochemical methods, the samples are placed as cathode and anode, respectively. So, it can be expected that formation mechanism of coatings alongside the resulting properties of the coatings must be different. In this section, the coating mechanism through cathodic electrochemical methods at first and thereafter anodic electrochemical methods will be discussed.

### 2.1. *Phosphate coating formation mechanism via cathodic electrochemical method*

In cathodic electrochemical method, the sample is placed as cathode. Therefore, it can be expected that the hydrogen reduction (reaction 1) must be the main reaction on the sample.

$$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2 \uparrow . \tag{1}$$

By the hydrogen reduction at the surface of sample, pH value between the electrode and the electrolyte increases,[61] which leads to speeding up of insoluble phosphate deposits on the surface which can be written as

$$3\mathrm{Zn}^{2+} + 2\mathrm{H}_2\mathrm{PO}^{-4} + 4\mathrm{H}_2\mathrm{O} + 6\mathrm{e}^- \\ \rightarrow \mathrm{Zn}_3(\mathrm{PO}_4)_2 \cdot 4\mathrm{H2O} + 3\mathrm{H}_2. \tag{2}$$

In the case of manganese phosphate with the reduction of hydrogen ions on the surface of the cathode, the acidity value between cathode surface and electrolyte is reduced and the reaction for the formation of phosphate coating can be written as follows[62]:

In the interface of cathode and electrolyte, these reactions occur:

$$\mathrm{Mn}(\mathrm{H}_2\mathrm{PO}_4)_2 \rightarrow \mathrm{Mn}^{2+} + 2\mathrm{H}_2\mathrm{PO}_4^-, \tag{3}$$

$$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O. \tag{4}$$

And finally the following reaction will proceed on the cathode surface:

$$Mn^{2+} + HPO_4^{2-} + 2.25H_2O \rightarrow MnHPO_4 \cdot 2.25H_2O. \tag{5}$$

In order to find out the details of phosphate coating formation mechanism deposited by cathodic electrochemical method, the cathode surface potential changes need to be recorded during coating treatment. In general, the cathode surface potential change during coating reflects the nature of the reactions performed during the coating process. Figure 2 illustrates cathode surface potential changes during cathodic electrochemical method.[63]

It can be seen that formation of coating during phosphate cathode process can be divided into three distinct stages. They are as follows[64]:

- First stage: Changing potential from an initial value to a maximum value.
- Second stage: The maximum potential changes to a steady value.
- Third stage: Potential changes after steady value.

Potential changes in each stage represent the nature of the surface in each stage. In the first stage, steel surface potential changes to anodic value. Although potential changes into anodic state has been observed during the first stage of chemical phosphate process that resulted from released phosphoric acid corrosive attack,[65,66] the potential change in the electrochemical method is bigger such that it must not occur by released phosphoric acid corrosive attack. By considering the composition of the bath, working conditions and metal surface potential, there must be some reasons for high potential change in deposition of zinc metal on the cathode surface along with hydrogen evolution during cathodic electrochemical method.[63,67] High amount of applied cathodic current also confirmed this behavior.

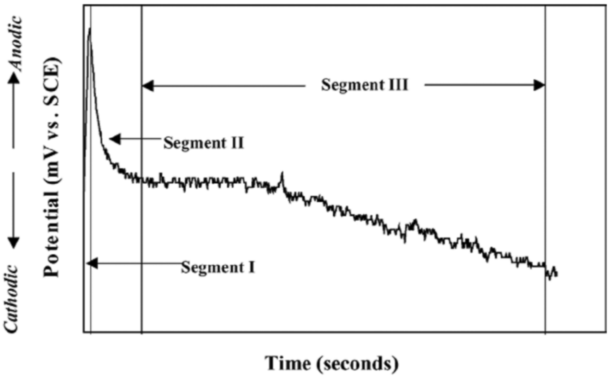


Fig. 2. A typical potential–time curve depicting the classification of three different segments of the curve to analyze the changes that occur during the cathodic phosphating process (see Ref. 63).

Second stage indicates potential changes from a maximum value to cathodic direction until it reaches a steady state value. Potential changes in cathodic direction can also be seen in the process of chemical phosphating because of the deposit on non-metal phosphate coating. Nevertheless, potential changes in the cathodic direction, in the cathodic operation, is only 50 mV which indicates that it is possible for zinc phosphate and zinc metal to precipitate at this stage simultaneously. However, the main reaction at this stage is zinc phosphate deposition.[63] Potential stability indicated at the end of second stage is due to sudden drop in conversion rate of changing initial phosphate to tertiary phosphate and also reduction in the rate of hydrogen evolution and zinc deposition.[67]

Third stage shows potential changes between initial stability point and deposition at the last stage and it also covers a big area of potential–time diagram, and simultaneous deposits of zinc and zinc phosphate are observed in this stage. Process variables such as current density, pH, and bath temperature determine the proportion of zinc phosphate to elemental zinc. Potential changes to anodic state prepare the conditions for zinc deposition and potential changes to the cathodic direction provide conditions for the zinc phosphate deposition.[63,67] According to potential–time measurement during cathodic electrochemical method, coating formation mechanism is proposed as follows:

During the initial stages, a thin layer of zinc is deposited on sublayer where hydrogen reduction occurred at the same time. Consumption of available hydrogen leads to pH increase in the interface of electrode–electrolyte and also eases the deposition of insoluble tertiary phosphate. Therefore, zinc phosphate deposition is placed on a thin layer of zinc coating. Continuous deposition of zinc eases the deposition of zinc phosphate on one sided area through reduction of hydrogen. As the coating process advances, available metal (zinc) is reduced to an

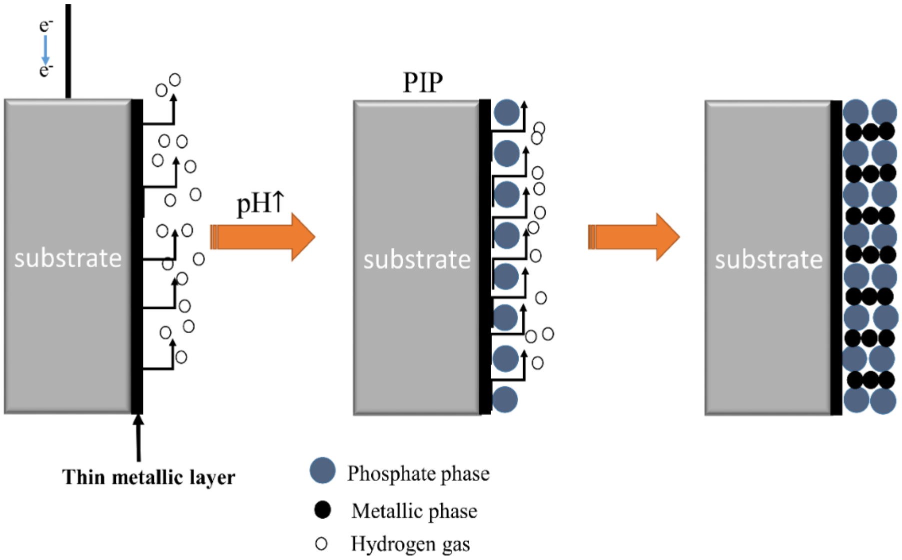


Fig. 3. Different stages of coating formation by cathodic electrochemical method.

almost constant value. Continuous release of hydrogen (which can be seen in all stages of coating) indicates the availability of metal places in the entire process time. It is recommended that zinc deposition should be developed across the coating thickness in the form of channels replete with non-metal zinc phosphate.[68] According to the above theory, a model image of the phosphate coating on the cathodic action is presented in Fig. 3. The zinc channels formed during the cross-section of the phosphate coating produced by cathodic electrochemical method are also shown in Fig. 4.[69] It can be seen that the simultaneous deposition of metal and non-metal phase occurs in cathodic electrochemical method. Therefore, the phosphate coating obtained via cathodic electrochemical method can be called phosphate composite coating. Other cations can also be used in the electrolyte to obtain different phosphate composite coating. Barati *et al.*[70] applied zinc–nickel phosphate composite coating on galvanized steel by employing cathodic electrochemical method and concluded that nickel and nickel phosphate with zinc phosphate are deposited on the surface of galvanized steel at the same time. Narayanan *et al.*[59] has also created zinc–iron composite phosphate coating by using steel anode during the dissolution of the coating and releases iron ions. Oskuie *et al.*[71] applied phosphate composite coating by utilizing three cationic phosphate bath and cathodic electrochemical method.

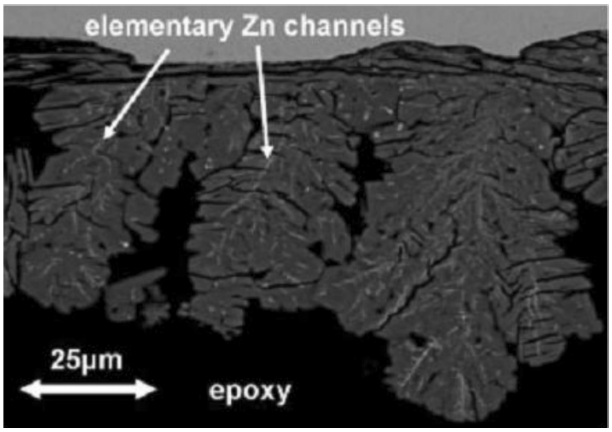


Fig. 4. SEM cross-section photograph of an electrodeposited Hopeite layer, which is pervaded by bright Zn-channels (see Ref. 69).

## 2.2. *Phosphate coating mechanism formation through anodic electrochemical method*

During the operation of anodic electrochemical method, anode is considered as the base metal and resolved in bath by applying anodic current. Hydrogen reduction reaction occurs in the cathode (counter electrode). Anodic reaction is the substrate dissolution. As mentioned earlier, the increase in pH in the interface is the important background for deposition of insoluble phosphate coating on the base metal surface. In anodic phosphating process, the majority of resolved sublayer ions that are available at the interface ease proton movement from the interface to the bulk of solution that leads to pH increase at the interface. So the phosphate coating is created on the surface of the steel. The value of resolved metal is increased intensively by current density and temperature rise, however, increase in coating weight is less due to reenergized phosphoric acid which is caused by changing initial phosphate to tertiary phosphate because this reality increases local acidity at the interface, so this acid can attack base metal and coating and result in coating resolve.[45,46] Potential–time change diagram during anodic electrochemical process is shown in Fig. 5 which demonstrates two stages, where in the first stage, the potential of substrate metal is increased in anodic direction. Potential change in anodic direction is observed in chemical phosphating in this stage. Potential change in this stage in anodic phosphate process is due to decrease of $H^+$ ions at the interface between electrode and electrolyte which is through the force imposed by iron ions on protons that results in potential changes in anodic direction. Therefore, dissolution of base metal is the main reaction at the initial stage and the second stage includes potential changes from a maximum value to a less value. Potential changes in cathodic direction in this stage can also be observed during chemical phosphate conversion due to deposition of zinc phosphate. Therefore, potential change at this stage in anodic electrochemical method is due to deposition of zinc phosphate. Maximum value of potential reflects the start of initial solution phosphate conversing to insoluble tertiary phosphate. More potential change in cathodic direction is a function of current density, pH and bath temperature.[45,46]

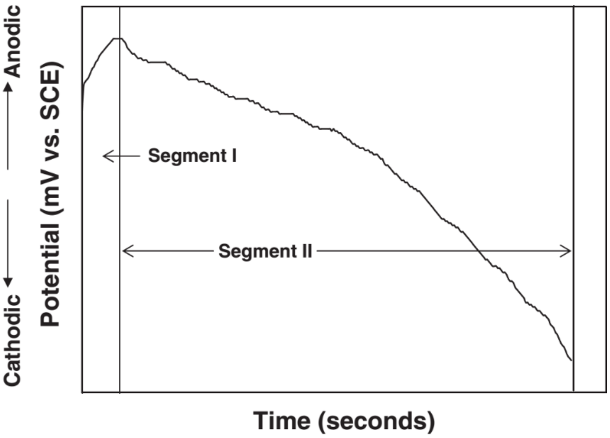
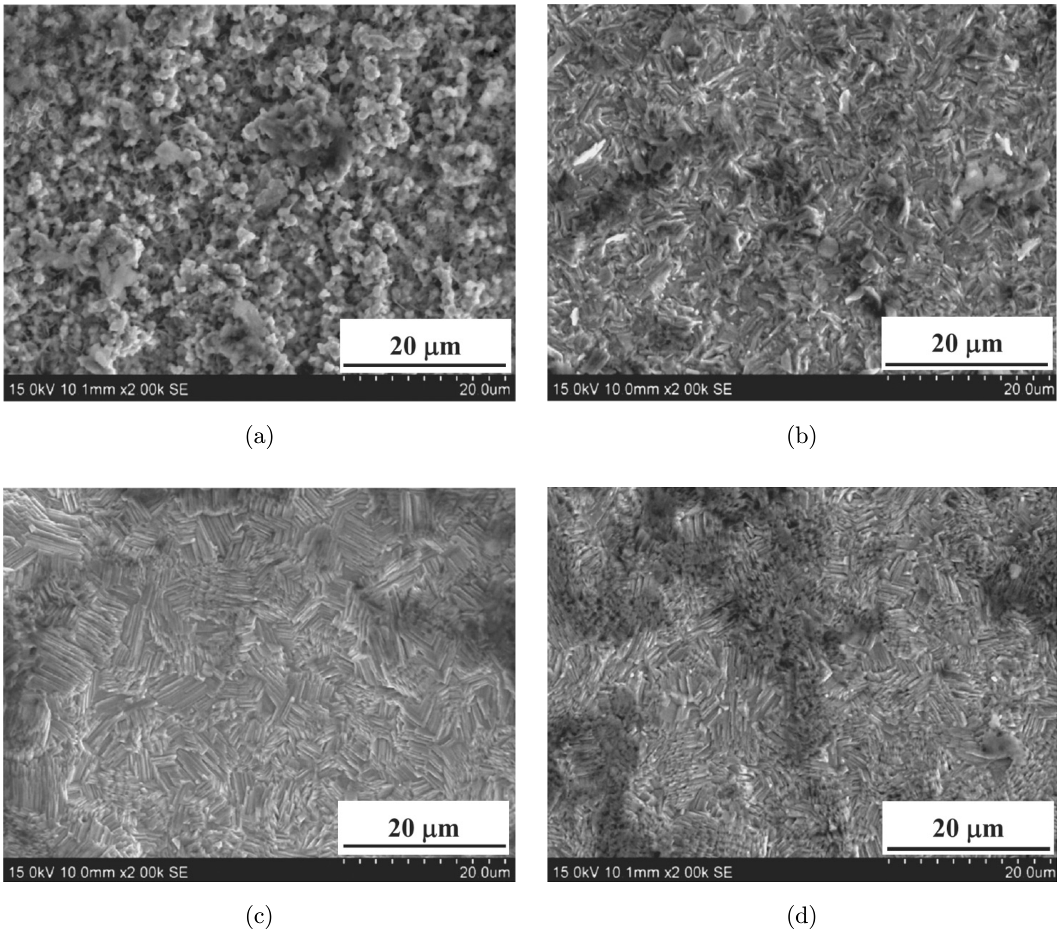


Fig. 5. A typical potential–time curve depicting the classification of the two different segments of the curve to analyze the changes that occur during anodic phosphating process (see Ref. 46).

## 3. Characteristics of Phosphate Coatings Fabricated Using Electrochemical Methods

### 3.1. *Composition and microstructure of coating*

Generally, during cathodic electrochemical operations, the applied cathodic current will accelerate the coating formation and also the application of cathodic current prevents the dissolution of the substrate and forms a coating with high density and high uniformity. Barati *et al.*[70] demonstrated that zinc–nickel phosphate composite coating generated via cathodic electrochemical reaction is dense and its crystals are in flower-like and plate-like form. Flower-like and plate-like crystals are a sign of Hopeite, reported by Jegannathan *et al.*[63] and Kuwait *et al.*[68] Figure 6 illustrates phosphate composite coating on aluminum substrates at various current densities. It can be seen that needle-like and flower-like crystals can be seen in current density of $10\,\mathrm{mA/cm^2}$. The formation of needle-like[69,72,73] and flower-like[74] phosphate crystals have also been observed by other researchers in the conventional chemical phosphating method. So, it can be concluded that regardless of the type of coating formation, the morphology of zinc-based phosphate coatings has the form of needle or flower-like crystals. As can be seen in Fig. 6, by increasing the applied current density, coating morphology changes. This reality is due to augment in ions deposition with increase in coating current density and enriching of coating by zinc. Moreover, it is obvious that the size of coating crystals is increased as the coating current density intensified. The morphological changes in the coating, which is fabricated by cathodic electrochemical method, had been observed by adding additives. It is reported that by adding nickel ions to coating bath, plate-shaped crystals are formed.[70] Phosphate coating morphology changes by the addition of niobium, ammonium oxalate and benzotriazole which is also observed in conventional chemical phosphating method.[75]



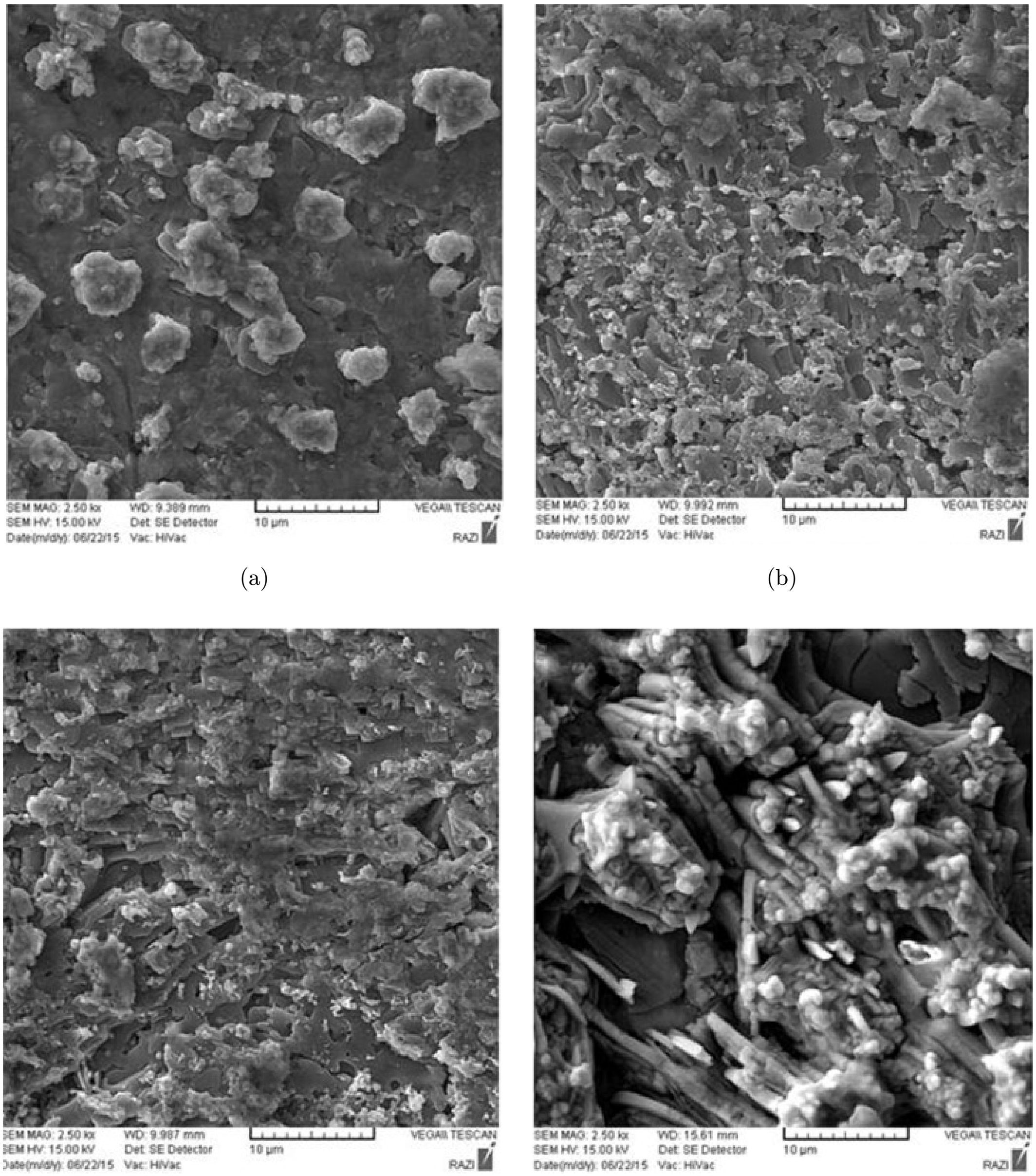
(a) (b)

(c) (d)

Fig. 6. Scanning electron microscopic images of zinc–zinc phosphate coatings deposited on Al by cathodic electrochemical treatment as a function of current density: (a) 10 mA/cm$^2$; (b) 20 mA/cm$^2$; (c) 30 mA/cm$^2$ and (d) 40 mA/cm$^2$. (Experimental conditions: ZnO: 5 g/l; $H_3PO_4$: 12 ml/L; pH: 1.5; current density: variable; temperature: 27 ± 1°C; Time: 30 min, see Ref. 68.)

The iron–manganese phosphate composite coating through cathodic electrochemical method revealed that the coating is dense and uniform, and the crystals of created coating are plane-shaped and disk-shaped.[62] A similar morphology was also observed in chemical manganese phosphating method.[76,77] Sponge-shaped crystals have been observed in iron–manganese phosphate composite coating, such that after the ESD analysis, it was seen that they are in fact manganese–iron phosphate crystals.[62] Plate-like crystals in magnesium phosphate coating applied via cathodic electrochemical method has been reported by Dayyari *et al.*[78] Arthanareeswari *et al.*[79] showed that creating a galvanic coupling for accelerating the formation of phosphate coating leads to increase in the rate of phosphate coating formation and reduces the size of the phosphate coating crystals. By comparing the coupled and uncoupled phosphate coating, they demonstrated that galvanic coupling increases the concentration of coat crystals.

Since in the anodic electrochemical method, the sample surface is polarized in anodic direction, the dissolution of the sample surface occurs, resulting in porosity augment. Barati *et al.*[70] demonstrated that utilizing anodic electrochemical method, the coating with high porosity and low density will be created and also indicated that only the flower-like crystals that are indicative of Hopeite will arise during the coating formation process. Phosphate coating obtained by anodic electrochemical method at various current densities is indicated in Fig. 7, as can be seen, only flower-like crystals appear in the coating and the



(a)

(b)

(c)

(d)

Fig. 7. SEM micrograph of Zn–Ni electrophosphate coating obtained by the anodic electrochemical method at different current densities: (a) 5, (b) 15, (c) 25 and (d) 35 mA/cm$^2$ (see Ref. 70).

porosity of the coating is higher than those fabricated by cathodic electrochemical method.

As mentioned earlier, in the cathodic electrochemical method, metallic and non-metallic phases deposit simultaneously on the surface, therefore it is expected that they exist as elemental form in the microstructure of coating. X-ray diffraction spectrum of the zinc–nickel composite phosphate coating obtained utilizing cathodic electrochemical method is shown in Fig. 8. It can be seen that zinc and nickel phase with nickel phosphate and Hopeite exist in the spectrum, this suggests the simultaneous presence of metallic and non-metallic phases in the coating. Simultaneous presence of metallic and non-metallic phases has not been observed in chemical phosphating. Simultaneous presence of metallic and non-metallic phases in phosphating through cathodic electrochemical method has been reported by other

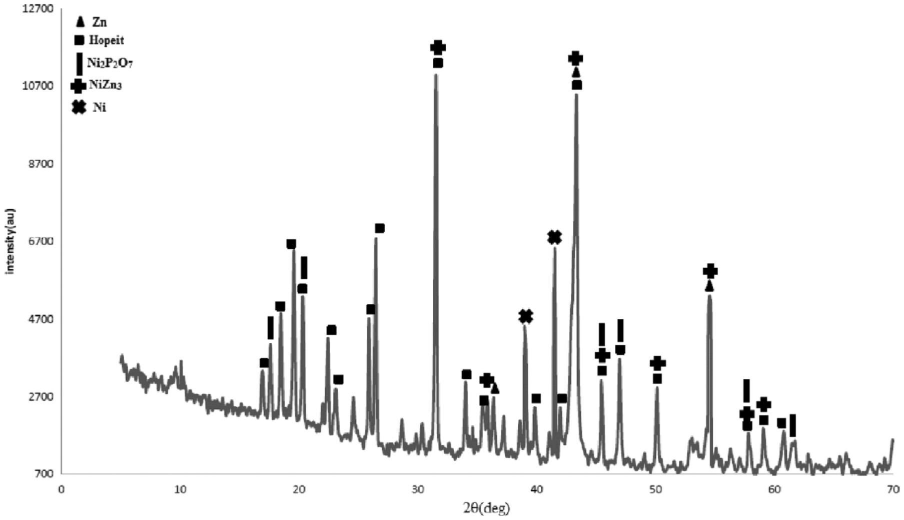


Fig. 8. XRD pattern of coating obtained by the cathodic electrochemical method (see Ref. 58).

researchers. The existence of metal iron magnesium phosphate phase in the chemical phosphating method of magnesium was studied by Fouladi *et al.*[80] and it was reported that the presence of iron phase is due to substrate. In the anodic electrochemical method, due to the dissolution of the substrate, metallic phase cannot be presented concurrently with non-metal phase in the microstructure of coating.

### 3.2. *Weight and thickness of coating*

The amount of deposited coating is one of the important properties of phosphate coatings that is considered in many standards as criteria of coating quality. In phosphating processes, coating thickness is usually expressed as mass per area unit which is generally called coating weight.[25] In the phosphating process, the pH value in the interface between the electrode and the electrolyte should be increased to create conditions for the formation of insoluble phosphate and coating. During the chemical phosphate coating methods, increase of interface pH that is controlled by influence of hydrogen ions via coating holes limits the amount of deposited coating, while in the cathodic electrochemical method, the simultaneous deposition of zinc along with zinc phosphate make the coating thicker. It was reported that by applying 50 mA/cm$^2$ for 30 min, a coating with 180 g/m$^2$ will be created.[68] While in chemical phosphating method, the augment of coating weight is 5–10 g/m$^2$.[81,82] Different factors like electrolyte pH, applied current density and coating time are effective on deposited amount. Kavitha *et al.*[68] investigated the effect of coating current density and bath pH on the amount of deposited coating. Coating weight change as a function of coating current density in different pH values is illustrated in Fig. 9. It can be seen that the coating value is increased linearly in pH from 1.5 to 2.3 and then it reaches a constant value, but the amount of coating deposited is due to en-

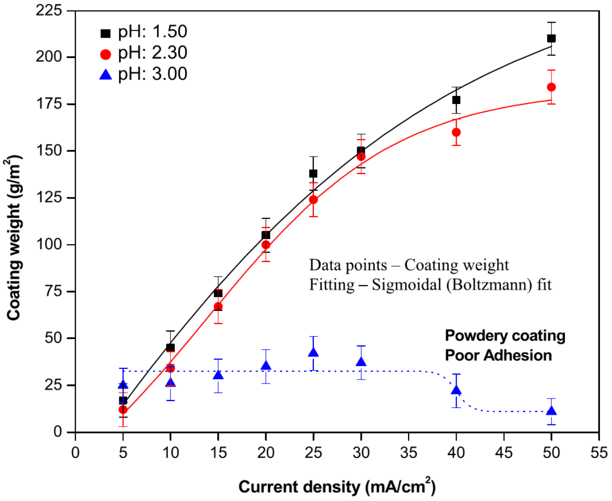


Fig. 9. (Color online) Variation in the amount of coating deposited during cathodic electrochemical treatment of Al as a function of applied current density as well as pH of the electrolyte. (Experimental conditions: ZnO: 5 g/l; $H_3PO_4$: 12 ml/L; pH: 1.50, 2.30 and 3.00; current density: 5–50 mA/cm$^2$; temperature: 27 ± 1°C; time: 30 min, see Ref. 68.)

hancement in the coating driving force due to the applied current density. In pH = 3, the amount of deposited coating is less due to the powdery state of coating in this stage. Weight loss of coating according to bath pH augment to a critical value has been seen in chemical phosphating.[56] It has also been reported that in phosphate process in cathodic electrochemical method, the amount of deposited coating is increased linearly until 50 min and then it reaches a constant value.[60]

### 3.3. *Corrosion behavior of coating*

By using cathodic electrochemical method, qualified phosphate coating with high corrosion resistance is achieved. Since in the cathodic electrochemical method, metallic and non-metal phases are deposited at the same time, corrosion behavior of this coating is interesting. Jeganathan *et al.*[63] surveyed corrosion resistance behavior of zinc phosphate composite coating through immersion test and concluded that in the surface of created coating, there is no sign of red color. This issue illustrates that this coating is uniform and has high corrosion resistance. One of the interesting observations in immersion test was the white corrosion products in phosphate coating. The reason for this event is due to the existence of zinc in metallic state in the coating structure. So, it can be concluded that phosphate coating created through cathodic electrochemical method is protected by two ways including sacrificial effect, which occurs with zinc in microstructure, and corrosive ion prevention into substrate which is provided by phosphate crystals.

Corrosion behavior evaluation for phosphate coatings created through cathodic electrochemical method carried out by electrochemical impedance spectroscopy demonstrates that the corrosion behavior of this coating is much different in comparison to phosphate coating created through usual chemical methods. In Nyquist curve of coatings through chemical method, a semicircular high frequency and a diffusion tail in low frequency[83] was created which shows that the corrosion behavior of these coatings is controlled by diffusion, while in the coating fabricated via cathodic electrochemical method, a small semicircular with an inductive loop is viewed and the first semicircular is related to zinc dissolution.[67] Therefore, it can be concluded that in electrochemical impedance spectroscopy test, zinc resolve is the main reaction in the initial stages of immersion. Thereafter, non-metal nature of coating was enhanced by increasing corrosion products. This event leads to increase in corrosion resistance with increase in immersion time.[59] Increase in corrosion resistance of coating due to increase in immersion time made by corrosion products has been investigated in another study.[60] Florian *et al.*[69] investigated corrosion resistance of phosphate coating fabricated by cathodic electrochemical method and the results demonstrated that corrosion resistance of this coating is due to reactions among steel substrate, electrophosphate and electrolyte and these reactions lead to improvement in corrosion resistance. In neutral solution, emergence of new layer is due to the barrier of zinc hydroxide on phosphate and steel interface which resulted in coating pores filling and consequently improvement in corrosion resistance behavior. The reactions of zinc hydroxide formation in neutral solution are as follows:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-, \tag{6}$$

$$PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^-, \tag{7}$$

$$HPO_4^{2-} + H2O \rightarrow H_2PO_4^- + OH^-, \tag{8}$$

$$Zn_3(PO_4)_2 + 6OH^- \rightarrow 3Zn(OH)_2 + 2PO_4^{3-}. \tag{9}$$

The comparison between corrosion resistance of coatings created through cathodic and anodic electrochemical methods has been carried out by Jeganathan *et al.*[45] The results of this study revealed that corrosion resistance of coatings created through anodic electrochemical method is similar to corrosion resistance caused by chemical method. Generally, it was concluded that corrosion resistance of fabricated coatings by cathodic electrochemical method is more than that of anodic electrochemical method. Some similar outcomes have also been reported by other researchers.[70] Creating phosphate composite magnesium–iron coating on aluminum through cathodic electrochemical method revealed that these kinds of coatings lead to the enhancement of corrosion resistance of substrate.[62]

Florica *et al.*[84] evaluated the ability of phosphate coating created by cathodic electrochemical method in order to protect mild steel against local corrosion caused by chloride ions in alkaline environment. Corrosion resistance evaluated by using open circuit potential, potentiodynamic polymerization and electrochemical impedance spectroscopy. The results of this study showed that slow resolve of coating leads to creation calcium hydroxyzincate phase and it was also obvious that after immersion for a long time in alkaline solution with or without chloride, the coating becomes dense and leads to improvement of substrate corrosion resistance.

Evaluation of corrosion resistance of phosphate coating created on steel through galvanic couple with titanium, nickel, copper and stainless steel was carried out by Arthanareeswari *et al.*[85,86] Evaluation of corrosion resistance through chemical stability test showed that fabricated coating through galvanic couple has the better corrosion resistance rather than that without galvanic coating.

## 4. Potential Applications of Coatings

Based on the properties of coatings fabricated by cathodic and anodic electrochemical methods, potential applications can be proposed for these coatings. Due to high porosity of anodic electrochemical coatings, these coatings can be manipulated for tube and wire drawing operations where high porosity is an advantage, also these coatings can be used as pretreatment for increase in paint adhesion to underlying metal. But due to high compactness of coatings fabricated by cathodic electrochemical method, these coatings can be applied for increasing corrosion resistance of underlying metals.

## 5. Concluding Remarks and Future Trend

The mechanism, microstructure, composition and corrosion resistance of phosphate coating created by electrochemical methods had been reviewed in this article. The results showed that mechanism of electrophosphate coating is different from the usual chemical phosphate coating and this reality leads to various coating properties. Evaluation of coating mechanism showed that metallic and non-metallic phases created through cathodic electrochemical method are present simultaneously, so this results in corrosion resistance improvement and porosity reduction. Applying current in this manner leads to enhancement in driving force of coating formation which provides a situation to achieve a thicker coating in less time. Moreover, by using this method, many of the toxic accelerators of electrolyte eliminated from bath lead to less harm to the environment.

By considering the mentioned subjects and increasing the need for energy consumption reduction and achieving favorite properties with less cost in less time, it is expected that more studies should be carried out on these kinds of coatings. Recommended studies for future works can be more precise on surveying of coating mechanism formation by utilizing more accurate and step by step studies and also using different cations to create phosphate composite coatings. Entering different cations at the same time in electrolyte and creating multi-cation coatings and surveying the resulting properties of these coatings can be the subject for future studies.

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