

## Electrochemical behaviour and analysis of Zn-Ni alloy anti-corrosive coatings deposited from citrate baths

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**Abstract.** Zinc-Nickel alloy coatings have been widely used to improve the corrosion resistance of steels. Electrodeposition of zinc-nickel alloy films on a steel plate under various deposition conditions is studied. The effects of plating variables such as bath composition, pH and current density on the coating composition, morphology and corrosion property have been systematically investigated. The zinc and nickel ions in plating baths are stabilized using complexing agent potassium citrate. Increasing the molar concentration of potassium citrate extends the pH of nickel hydroxide and zinc oxide precipitation. The morphological properties and crystalline phase structure of the deposited alloy coatings are examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The analyses reveal that the coatings deposited from citrate bath contain  $\gamma$ -NiZn<sub>3</sub> and  $\gamma$ -Ni<sub>2</sub>Zn<sub>11</sub> alloy phases. These phases improve the corrosion resistance of the steel plate. Electrochemical behaviour analyses of the Zn-Ni film illustrated by electrochemical impedance spectroscopy (EIS) measurement revealed that the sample (a) deposited from 0.0326M citrate bath at acidic pH shown higher impedance modulus than non-citrate bath coated samples, which improved anti-corrosive properties of the coatings. This study confirms that uniform Zn-Ni coating with smaller grain sizes has better anti-corrosive properties.

### 1. Introduction

Corrosion is one of the major causes of equipment failure and safety problems in offshore and marine operations, automobiles and aircraft industries[1,2]. The anti-corrosive coating is an effective approach for protecting the steel structures/machinery against corrosion [2]. The zinc-nickel alloy coatings are extensively employed in anti-corrosion purposes. Electrodeposition is one of the most widely applied technologies for the fabrication of corrosion resistant metallic coatings due to high technological feasibility and economic viability[3]. Zinc alloy coatings such as Zn-Ni, Zn-Cu and Zn-Fe alloy films are often used to provide excellent corrosion resistance and maintain good mechanical properties for steel parts or equipment. They have better corrosion resistance compared to pure zinc coating[4,5]. Electrodeposition is one of the most economical and conventional technologies for producing metallic coatings. The challenges for Zn and Zn alloy electrodeposition are hydrogen evolution and bath stability. The Zn alloy coatings deposited from citrate bath have been studied by Silva et al. (2010). They deposited Cu-Zn alloy coating on mild steel substrate from a bath containing sodium citrate as a complexing agent and benzotriazole and cysteine as additives. The results demonstrated that the coatings obtained with additives were brighter with small grain size. Cystine in the electrodeposition bath increases the potential for hydrogen evolution reaction (HER) and also prevents direct zinc deposition, and the deposited film exhibits high corrosion resistance[6].

Nowadays, Zn-Ni alloy coatings are the crucial eco-friendly substitute for toxic cadmium coating [7] and have attracted significant attention due to providing better corrosion resistance and mechanical properties at higher temperatures and severe environmental conditions, compared to pure zinc and other zinc alloy coatings [8]. Several analyses have been undertaken to understand the characteristics of the electrodeposition process of Zn-Ni alloys. It is found that the features of the deposited coating depend on the current density, pH, bath composition, applied voltage, additives and temperature[6].



The chemical composition, phase formation and microstructure of the deposited Zn-Ni alloy are essential characteristics which control corrosion resistance and other mechanical properties[7, 8].

As seen from the previous research, there are several experimental studies have been done on the Zn-Ni deposited from citrate bath at various operating parameters. To the best of the author's knowledge, there is no systematic study specifically Zn-Ni alloy at higher concentration of citrate, optimum parameter condition and challenge to suppress the hydrogen evolution reaction (HER) to improve corrosion resistant properties of the coating. Therefore, in order to fulfil this gap, the present research is to utilize the incremental study on the Zn-Ni alloy deposited at higher level operating conditions is investigated and analyzed.

The aim of this work is to electrodeposit Zn-Ni alloy films on steel substrates to improve corrosion resistance properties using potassium citrate as a complexing agent. The effects of plating variables such as bath composition, pH and current density on coating composition, morphology and corrosion property are investigated. The stability of Zn-Ni plating bath and suppression of HER are examined. The electrochemical behaviour of the deposited Zn-Ni alloy coatings is also analyzed.

## 2. Experimental methods

The electrodeposition experiments were carried out in a bath cell with the 200ml solution at room temperature. A rectangular steel plate of 10 cm<sup>2</sup> was used as the working electrode (cathode), and a graphite rod was used as the counter electrode (anode). The anode and cathode were connected to the D.C power supply via a multi-meter. There were two types of baths prepared as shown in Table 1. The pH of the bath was adjusted to acidic using hydrochloric acid. The agitation speed was 350 rpm and the electroplating time was 10 min. The steel plates for electroplating were polished by 400, 600, and 800 grit papers. They were degreased with 10 wt% sodium hydroxide solution for 5 min, then rinsed with 10 wt% hydrochloric acid and alcohol for a few seconds. The conditions for electrodeposition are listed in Table 2. After deposition, the Zn-Ni alloy coatings were washed with distilled water and dried in air. The stability of the baths was calculated using OLI software. Electrochemical analyses were performed using a ZAHNER IM6 electrochemical workstation produced by ZAHNER-Elektrik GmbH & Co.KG, Germany. The electrochemical analysis experiments were carried out in a conventional three-electrode cell with the 200ml solution. A 10 cm<sup>2</sup> rectangular steel plate was used as the cathode. A graphite rod was used as the anode. Silver/silver chloride electrode with saturated potassium chloride salt bridge (Ag/AgCl/KCl<sub>sat</sub>) was used as the reference electrode. The morphology of the deposited samples was investigated by scanning electron microscopy (FEI MLA 650F). A Rigaku Ultima IV X-ray diffractometer with a copper x-ray source and a scintillation counter detector was used to study the crystal phase structures of deposits, and the databases used to identify the peaks were pdf# 03-065-5310 and 00-004-0831 RDB Minerals, International Centre for Diffraction Database (ICDD).

**Table 1.** Bath compositions for the electrodeposition of Zn-Ni alloy coatings

Bath Composition	Molar Concentrations	
	Bath-1	Bath-2
Zinc Chloride (ZnCl <sub>2</sub> )	0.550M	0.550M
Nickel (II) chloride hexahydrate (NiCl <sub>2</sub> .6H <sub>2</sub> O)	0.105M	0.105M
Boric Acid (H <sub>3</sub> BO <sub>3</sub> )	-	0.161M
Sodium dodecyl sulfate (SDS)	0.000017M	0.000017M
Potassium Citrate (K <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ))	-	0.0326M
Sodium chloride (NaCl)	0.171M	0.171M

**Table 2.** Conditions for depositing the Zn-Ni alloy coatings

Bath conditions	Samples	pH range of bath
Bath-1 (with 0.0326M potassium citrate)	(a)	Acidic (pH=2.5)
	(c)	Natural (pH=5.5)
Bath-2 (without potassium citrate)	(b)	Acidic (pH=2.5)
	(d)	Natural (pH=5.5)

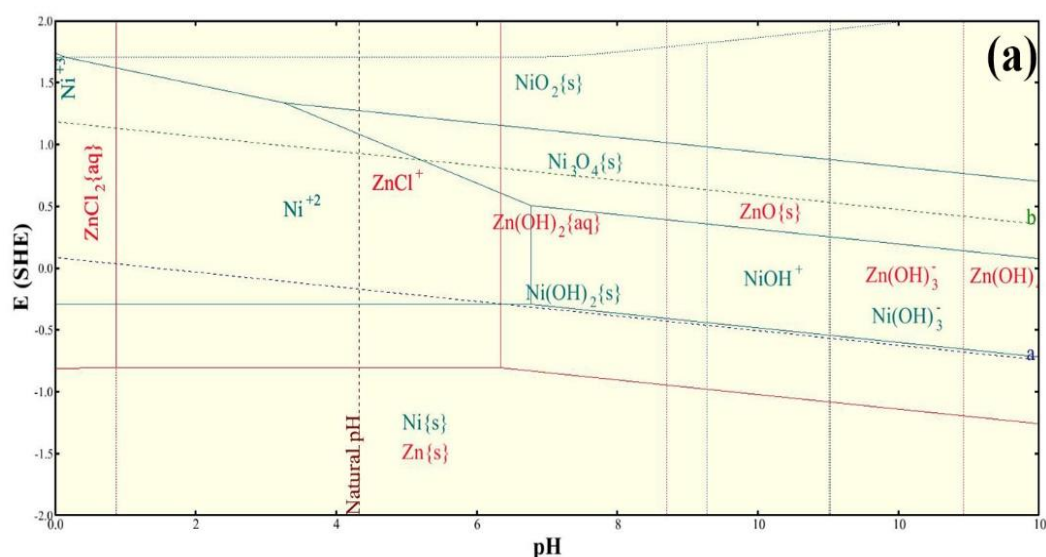
### 3. Results and Discussion

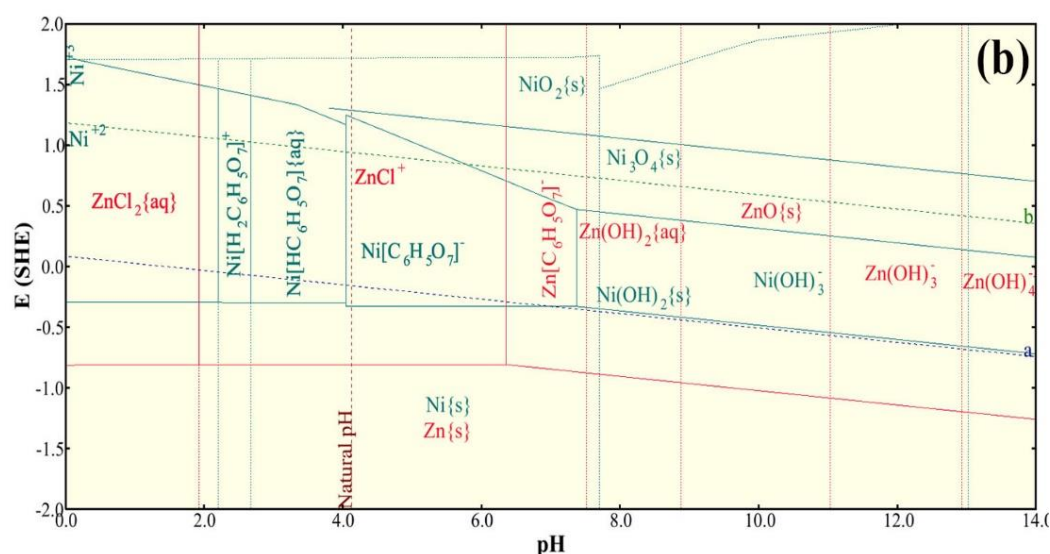
#### 3.1. Effect of complexing agent on the stability of plating bath

The stability of an electroplating bath can be studied through the stability diagram or Pourbaix diagram. Complexing agents such as potassium citrate were employed to stabilize the metal and alloy plating baths. Figures 1 (a) and (b) are the pourbaix diagrams calculated for the Zn-Ni alloy plating baths without the addition of potassium citrate and with the addition of 0.0326M potassium citrate.

It can be seen that, thermodynamically, the stability of a Zn-Ni alloy plating bath is dominated by the precipitation of  $\text{Ni(OH)}_2$  and  $\text{ZnO}$  at pH 6.8 and 8.6, respectively (Figure 1a). After the addition of 0.0326M of potassium citrate, the Zn-Ni alloy plating bath is thermodynamically stable until pH 7.8 for  $\text{Ni(OH)}_2$  precipitation due to the formation of stable complexing species  $\text{Ni}[\text{C}_6\text{H}_5\text{O}_7]^-$ , and  $\text{ZnO}$  precipitates out at pH over 8.7 with the given concentration of metal ions (Figure 1b).

The calculated stability diagrams demonstrate that, thermodynamically, citrate can efficiently stabilize Zn-Ni alloy plating baths, preventing the precipitation of metal hydroxides at a higher pH.





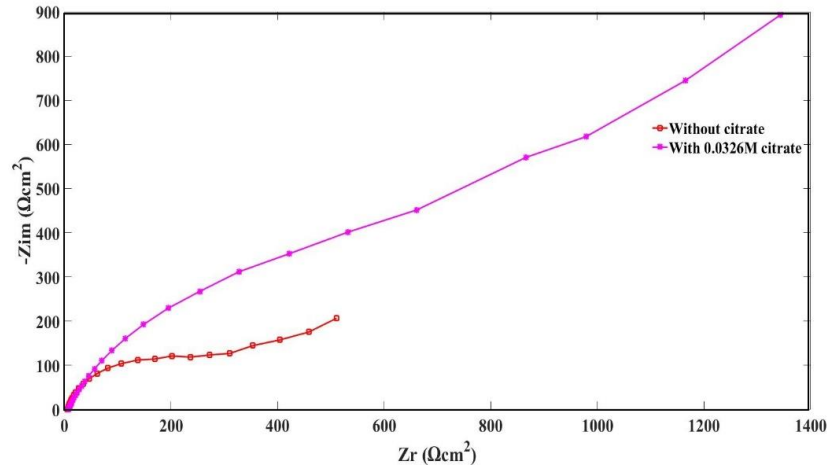
**Figure 1 (a).** The Pourbaix diagram for Zn-Ni alloy plating bath without the addition of  $K_3(C_6H_5O_7)$  (Bath-1). The dashed lines 'a' and 'b' refer to the equilibrium lines for  $H^+/H_2$  and  $(O_2+H_2O)/OH^-$  respectively, as they do in Figure 1b. **(b).** The Pourbaix diagram for Zn-Ni alloy plating bath with the addition of 0.0326M potassium citrate  $K_3(C_6H_5O_7)$  (Bath-2).

### 3.2. Electrochemical Impedance Spectroscopy (EIS) analysis

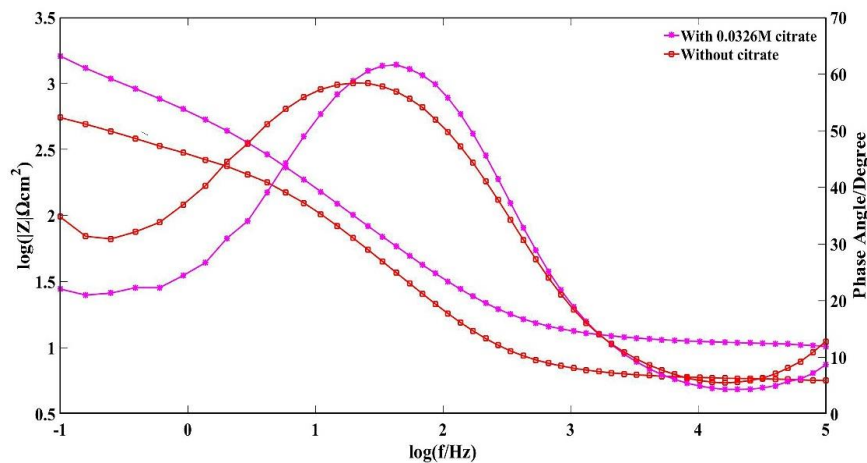
The Electrochemical Impedance Spectroscopy (EIS) measurement is used as a corrosion resistance analysis technique to evaluate the characteristics and kinetics of the electrochemical process prevailing at the electrode/solution interface in corrosive solutions[11,12]. The EIS measurements are carried out for the films deposited from citrate and non-citrate baths in a 3.5% NaCl solution to analyze the corrosion resistance behaviour of Zn-Ni coatings. The frequency range of open circuit potential (OCP) is 100kHz to 100mHz. The measured EIS data displayed as Nyquist and Bode plot are shown in Figures 3 and 4. In the Nyquist plots, the polarization resistance resembles the shape of a semicircle[13][14]. The EIS measurement of sample (a) deposited from 0.0326M citrate bath at acidic pH shown higher impedance modulus than the non-citrate bath coated samples. In the view of impedance vs frequency, impedance value increases by adding the potassium citrate. As for bode plots of frequency vs phase angle, phase angle also increases from citrate bath as shown in Figure 4.

The measuring setup for corrosion resistance of the presented Zn-Ni alloy coating can be explicated by an equivalent electrical circuit. The calculated fit data of the equivalent circuit for films deposited from citrate and non-citrate baths at acidic pH are listed in Table 3, where  $R_{sol}$  represents the solution/electrolyte resistance between the reference and working electrode (i.e., Zn-Ni coated specimen).  $R_3$  and  $CPE_3$  correspond to the resistance and capacitance of the formation of the thin oxide film that is reinforced by the ionic conduction through its pores.  $R_2$  and  $CPE_2$  correspond to the resistance and capacitance of the Zn-Ni alloy films.  $R_1$  represents the charge transfer resistance associated with the reaction of zinc oxide and reduction of oxygen.  $CPE_1$  corresponds the electric double layer capacitance at the interface of coating/electrolyte solution. All the measured impedance values were fitted using Zahner Thales software. The charge transfer resistance ( $R_1$ ) of the Zn-Ni coating is  $3.6 K\Omega cm^2$  from 0.0326M citrate bath, which illustrates that the higher oxide reduction and zinc oxidation occurring on the coated surface; while, for the non-citrate Zn-Ni alloy sample, the  $R_1$  value is  $688 \Omega cm^2$  due to the increase of the active surface. It is well known that higher polarization resistance ( $R_2$ ) values indicate better corrosion resistance. The decrease of  $R_2$  from  $879 \Omega cm^2$  to  $264 \Omega cm^2$  suggests the easier access of the electrolyte to the Zn-Ni coated surface deposited from non-citrate baths. Moreover, Zn-Ni coating deposited from non-citrate bath had lower  $R_1$  and  $R_2$ , which means that electrolyte diffused into the coating surface exhibit less corrosion resistance. Zn-Ni alloy from citrate bath had maximum coating resistance ( $R_2$ ) with minimum capacitance ( $CPE_2$ ) of  $879 \Omega cm^2$  and  $28.2 \mu F cm^2$ . This behaviour suggests that the addition of the complexing agent ( $K_3(C_6H_5O_7)$ ) in a bath is a practical approach to increase the corrosion resistance of Zn-Ni alloy

coating. Similar electrical equivalent circuit have been reported by Feng et al. (2016) prepared Zn-Ni alloy coating from a new DMH-based bath as a replacement of Zn and Cd coatings[15].



**Figure 2.** Nyquist plot for the Zn-Ni alloy coatings deposited from citrate and non-citrate baths at pH= acidic



**Figure 3.** Bode plot for the Zn-Ni alloy coatings deposited from citrate and non-citrate baths at pH= acidic

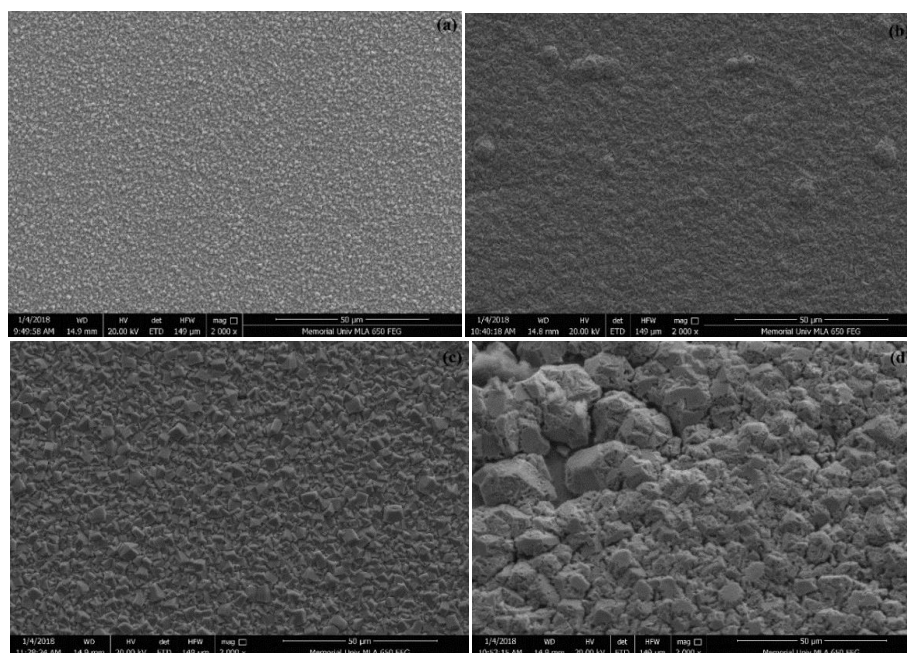
**Table 3.** Electrochemical parameters determined by equivalent circuit modelling

Bath condition	$R_{sol}$ ( $\Omega\text{cm}^2$ )	$R_1$ ( $\Omega\text{cm}^2$ )	$R_2$ ( $\Omega\text{cm}^2$ )	$R_3$ ( $\Omega\text{cm}^2$ )	$CPE_1$ ( $\mu\text{Fcm}^2$ )	$CPE_2$ ( $\mu\text{Fcm}^2$ )	$CPE_3$ ( $\text{nFcm}^2$ )
From citrate	3	3.6K	879	4.2	40	28	98
Non-citrate	2.6	688	264	3.3	106	64	104

### 3.3. Surface morphology and chemical compositions

The surface morphology of the Zn-Ni coatings deposited from citrate bath and non-citrate bath at different pH level was investigated using scanning electron microscopy (SEM) as shown in Figure 5. The deposited Zn-Ni alloy coating obtains different uniformity, porosity and grain size by varying bath compositions, current density and pH. All the images are taken at the same magnification. The sample (a) Zn-Ni alloy coating at a plating current density equal to 60 mA/cm<sup>2</sup> exhibits smaller and

more uniform grain sizes, and no swelling is found on the coatings. Rahman et al. (2009) reported that from 40-60mA/cm<sup>2</sup> plating current density grain of the deposit is smaller, uniform and no porosity is found whereas, with increasing plating, current density after 60mA/cm<sup>2</sup> have to produce non-uniform crystals and coarse-grained coatings[9]. Thus, the nature of the deposits is uniformly adherent and dense (Figure 4(a)). The sample (b) coating at same conditions reveals non-uniformity, swelling with larger and coarser grain sizes are found due to the HER. The sample (c) coating has bigger grain size and rough surfaces, the sample (d) coating has more massive coarse structure with some cracks.

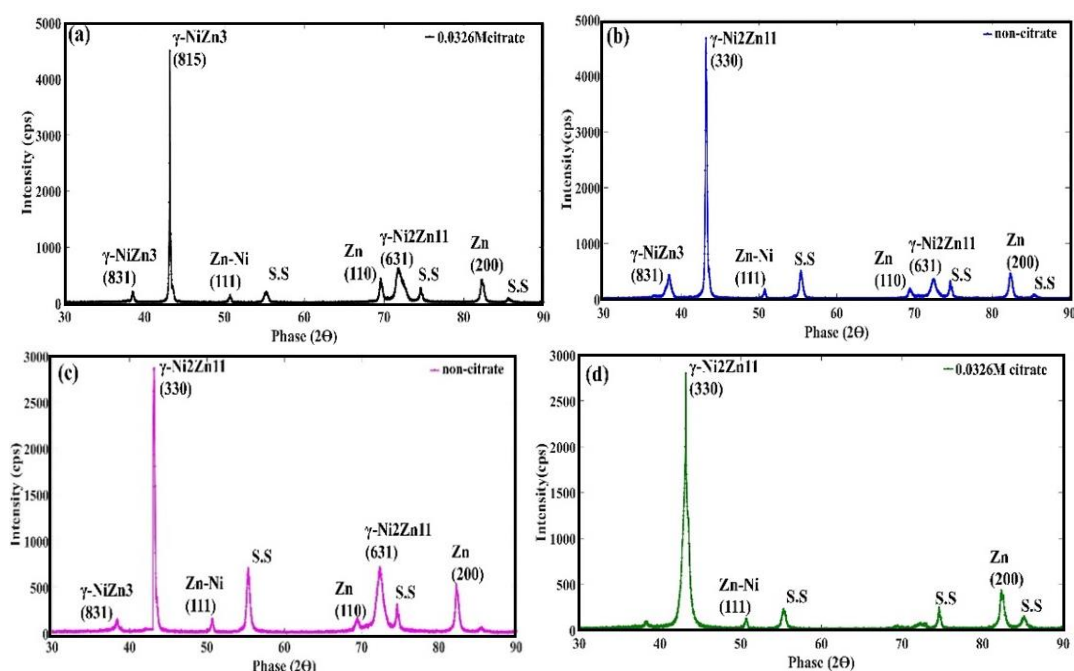


**Figure 4.** The SEM images of Zn-Ni alloy coatings (a) deposited from 0.0326M citrate at pH=acidic, (b) deposited from non-citrate at pH= acidic, (c) deposited from 0.0326M citrate at pH=natural, (d) deposited from non-citrate at pH=natural

### 3.4. X-Ray Diffraction (XRD) analysis

The XRD patterns distinguish the crystalline phases and orientation of the Zn-Ni coatings deposited at different conditions, as shown in Figure 6. The peaks around 38°, 43° and 73° correspond to  $\gamma$ -NiZn<sub>3</sub> (831) and  $\gamma$ -Ni<sub>2</sub>Zn<sub>11</sub> (330) (631) crystal planes. The other peaks are at 51°, 69° and 82° matching the Zn-Ni (111) and Zn (110) (200) planes. The Zn-Ni coating deposited from an acidic citrate bath has the highest intensity of the  $\gamma$ -phase ( $\gamma$ -Ni<sub>2</sub>Zn<sub>11</sub>) with (330) plane orientation, as shown in Figure 6 (b). Moreover, the peak value of  $\gamma$ -phase (330) plane is higher than those of other  $\gamma$ -phase orientations such as  $\gamma$ -NiZn<sub>3</sub>, demonstrating that  $\gamma$ -phase with (330) plane orientation is preferentially formed in the Zn-Ni alloy coatings[16][17][18]. The additives or complexing agents are adsorbed on the Zn-Ni matrix preferentially and inhibits Zn-Ni alloy depositions, resulting in the smaller reduction of Zn<sup>+2</sup> and Ni<sup>+2</sup> on these matrices, therefore smooth and homogeneous deposits can be observed[19]. The intensity of the  $\gamma$ -phase ( $\gamma$ -Ni<sub>2</sub>Zn<sub>11</sub>) of Sample (b) is high in comparison to other samples. In sample (a), the  $\gamma$ -Ni<sub>2</sub>Zn<sub>11</sub> peak is replaced by  $\gamma$ -NiZn<sub>3</sub> (815). Therefore, the coating with high-intensity  $\gamma$ -phase with (330) (815) plane orientation exhibits better corrosion resistance.





**Figure 5.** XRD patterns for the Zn-Ni alloy coatings (a) deposited from 0.0326M citrate at pH=acidic, (b) deposited from non-citrate bath at pH= acidic, (c) deposited from 0.0326M citrate at pH=natural, (d) deposited from non-citrate bath at pH=natural

#### 4. Conclusions

The electrochemical behaviour of Zn-Ni alloy coating from citrate and non-citrate bath are concluded as follows:

- Stabilized plating baths and complexing agents such as potassium citrate are employed for Zn-Ni alloy electrodeposition. This extends the precipitation of nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ), and zinc monoxide ( $\text{ZnO}$ ) to a higher pH and the hydrogen deposition is also suppressed.
- The EIS measurement of sample (a) deposited from 0.0326M citrate bath at acidic pH shown higher impedance modulus than the non-citrate bath coated samples.
- The electrical equivalent circuit modelling data best fit the generated Nyquist plot demonstrated that the Zn-Ni alloy coating on steel substrate deposited from citrate bath had maximum coating resistance ( $R_2$ ) with minimum capacitance ( $\text{CPE}_2$ ) of  $879 \Omega\text{cm}^2$  and  $28.2 \mu\text{Fcm}^2$ . This behaviour indicates that the addition of the complexing agent ( $\text{K}_3(\text{C}_6\text{H}_5\text{O}_7)$ ) in a bath is a simple and effective process to improve the corrosion resistance of Zn-Ni alloy coating.
- The equivalent electrical circuits obtained from the experimental fitted data also demonstrated the drastic change in charge transfer ( $R_1$ ) and polarization resistance ( $R_2$ ) occurring on the Zn-Ni alloy coated surface deposited from citrate in comparison to a non-citrate bath.
- The sample (a) Zn-Ni alloy coating at a plating current density equal to  $60 \text{ mA/cm}^2$  exhibits smaller and more uniform grain sizes, and no swelling is found on the coatings.
- The phase structure of the Zn-Ni deposit obtained from an acidic citrate bath having the highest intensity of  $\gamma\text{-NiZn}_3$  (815) and  $\gamma\text{-Ni}_2\text{Zn}_{11}$  (330) (631) planes exhibits better corrosion resistance.

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