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# **Influence of Electrodeposition Time on Corrosion Performance of Tinplate in NaCl Solution**

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The influence of electrodeposition time on corrosion performance of tinplate in 3.5 mass% NaCl solution has been investigated by electrochemical measurements and scanning electron microscope observation. The results indicate that tinplate obtained at 120 s electrodeposition time with a higher tin coating mass of  $11.2 \text{ g} \cdot \text{m}^{-2}$  exhibits better corrosion resistance than the sample obtained at 12 s electrodeposition time with a much lower tin coating mass of  $1.1 \text{ g} \cdot \text{m}^{-2}$ . The tin coating mass of the sample obtained at 12 s electrodeposition time with a much lower tin coating mass of  $1.1 \text{ g} \cdot \text{m}^{-2}$ . The tin coating mass of the sample obtained at 12 s electrodeposition time may not uniformly cover the steel substrate with surface roughness or other defects, and thus cannot provide enough protection ability to steel substrate in 3.5 mass% NaCl solution.

Keywords: Corrosion behavior; Tinplate; Tin-coating; Thickness; NaCl solution

## **1. INTRODUCTION**

Having become one of the dominant materials for food cans, tinplate is a light gauge, cold reduced, low-carbon steel sheet or strip, coated on both sides with commercially pure tin [1], combining the strength and formability of steel and the corrosion resistance with good appearance of tin [2]. The excellent ductility of tin coating makes the tinplate can be processed into various shapes without the coating destruction [3]. Tinplate is used in more than 80% of cases though the new alternative materials such as aluminum and chromated steel sheet are increasingly used by the canning industry [4]. At the same time, because of the lower tin reserves on the earth and the increasing demand for package material, the continuous reduction of tin mass has become a major trend for tinplate development to reduce the production cost and saving tin resources. At present, stable production of tinplate with lower tin coating mass has been achieved at some manufactures. For the protection of the steel plate, the tin coating must be non-porous; otherwise, the base steel will undergo severe corrosion in the humid air. Therefore, a tin coating thickness of at least 30  $\mu$ m is one general requirement used for food processing equipment or shipping containers [5]. The acid sulfate tin plating process was usually carried out in a temperature

range of 10–30 °C [6]. The Sn<sup>2+</sup> in acid plating solution has 2 times more electrochemical equivalent than that of Sn<sup>4+</sup> in the alkaline plating solution, and thus acid plating solution has a fast deposition speed and high current efficiency (close to 100%) [7]. The tin coating is on the order of several microns in thickness, though it is more usually defined in terms of tin coating mass ( $g \cdot m^{-2}$ ) [1]. Conventional tinplate is typically produced by initially electrodepositing a porous layer of pure tin (usually 2.8  $g \cdot m^{-2}$ – 11.2  $g \cdot m^{-2}$ ) onto the cathodic steel substrate and heating above the melting point of tin (reflowing) [8]. Reflowing causes the tin layer to become fully dense (bright tin) and also allows the creation of partial or complete iron-tin intermetallic, typically FeSn<sub>2</sub> [9].

Heretofore, the corrosion behavior of tin element or tin coating has been extensively investigated [10–14]. Wint *et al.* [10] carried out a systematic study into the initiation and propagation of cathodic delamination on pure iron, pure tin, and industrially important tin and iron-tin intermetallic (FeSn and FeSn<sub>2</sub>) coatings for packaging steels. Ha *et al.* [11] studied the role of Sn in corrosion and passive behavior of extruded Mg-5wt% Sn alloy in NaCl solution. Arazna [12] *et al.* investigated the corrosion characteristics and solderability of immersion tin coatings on copper. Zhong [13] *et al.* studied the corrosion rate increases as the electrolyte layer thickness decreases in the initial stage. Xia *et al.* [1,14] investigated the corrosion behavior of tinplates in functional beverage and NaCl solutions.

Recently the increasing price of tin in the commodities market has resulted in a need to reduce the amount of tin used in tinplate materials (about  $1 \text{ g} \cdot \text{m}^{-2}$  tin coating mass) whilst retaining adequate corrosion resistance. As to the selection of tinplate coating mass, it should be based on the practical application environment, i.e. corrosive environment. In a neutral solution, the corrosion rate and lifespan of tinplate are closely related to corrosive substance concentration. In acid solution, the pH value also affects the corrosion behavior of the tinplate. Therefore, the various and complicated corrosive environment contributes to the fact that it is difficult to point out the selection of coating mass in practical application. The principal purpose of tin coating on tinplate packaging materials is to provide corrosion resistance [15]. However, to our knowledge, less work has been done to investigate the influence of electrodeposition time on corrosion performance of tinplate in 3.5 mass% NaCl solution. Thus, the knowledge of corrosion, which can also provide a reference for a further study aiming to improve their corrosion resistance. The current investigation aims to study and discuss the influence of electrodeposition time on corrosion performance of tinplate in 3.5 mass% NaCl solution by electrodeposition time on corrosion performance of tinplate in 3.5 mass% NaCl solution the viewpoint of corrosion, which can also provide a reference for a further study aiming to improve their corrosion resistance. The current investigation aims to study and discuss the influence of electrodeposition time on corrosion performance of tinplate in 3.5 mass% NaCl solution by electrochemical measurements.

## **2. EXPERIMENTAL**

#### 2.1 Preparation of samples

The substrate for tinplate preparation is low carbon steel with a surface roughness of about 0.9  $\mu$ m. Before the electrodeposition process, the steel sheets were mechanically polished, cleaned in 10 wt.% NaOH solution maintained at 50 °C, and then immersed in alcohol to further remove any oils.

Details of the electrodeposition process can be found in Table 1 [15], and the coating mass is achieved by controlling the electrodeposition time at fixed current density. After the electrodeposition process, the obtained tinplate samples were then successively subjected to processes of reflowing treatment and passivation process, whose parameters can also be found in Table 1. In this investigation, four values of electrodeposition time of 12, 30, 60, 120 seconds were selected to investigate the influence of electrodeposition time on coating mass distribution and surface coverage during electrodeposition of tin on carbon steel. The tin coating mass can be calculated by Eq. (1) as follows:

$$m = \frac{A}{z \times F} I \times t \times 0.95 \tag{1}$$

where A is Sn atomic mass; z is  $Sn^{2+}$  valence; F is Faraday constant; I is Current density; t is deposition time, and 0.95 is current density efficiency. The obtained coating mass corresponding to electrodeposition time of 12, 30, 60, 120 seconds is 1.1, 2.8, 5.6, and 11.2 g m<sup>-2</sup>, respectively.

Process	Operation	Process parameters		Condition
Step 1	Polishing	Abrasive paper		
Step 2	Alkaline cleaning	NaOH	$100 \text{ g L}^{-1}$	50 °C, 10 min
		Absolute alcohol		
		SnSO <sub>4</sub>	$35 \text{ g L}^{-1}$	
		$H_2SO_4$	$180 \text{ g } \text{L}^{-1}$	
		Methyl sulfonic acid	$15 \text{ g L}^{-1}$	
Step 3		ENSA	$3.0 \text{ g L}^{-1}$	
		EN	$5.0 \text{ g L}^{-1}$	Temperature
		Fe <sup>2+</sup>	$< 7.0 \text{ g L}^{-1}$	25 °C
	Electrodeposition Sn	Sludge	$< 2.0 \text{ g L}^{-1}$	
	coating	$\mathrm{Sn}^{4+}$	$< 1.0 \text{ g L}^{-1}$	
		Anode	99.9 % Sn	
			12 s	Current density
		Electrodeposition	30 s	$2.0 \text{ A dm}^{-2}$
		time	60 s	(05% Efficiency)
			120 s	(95% Efficiency)
Step 4	Reflowing treatment	Temperature	235 °C	
		Time	10 s	
Step 5	Surface passivation	$Na_2Cr_2O_7$	$25 \mathrm{~g~L}^{-1}$	Temperature
	treatment	pH	4.4	42 °C
	treatment	Cathodic current		Moderate

Table 1. Processes and parameters for electrodeposition tin coating on low-carbon steel substrate

#### 2.2 Electrochemical measurements

The obtained tinplate samples with different coating mass were encapsulated using package adhesive sealant silicone rubber with an exposed area of  $1 \text{ cm}^2$  for the test, dried in a desiccator for 24 h, and then subjected to electrochemical measurements in 3.5 mass% NaCl solution.

The influence of electrodeposition time on corrosion performance of tinplate was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) at 25 °C through Gamry Reference 600 electrochemical workstation in 3.5 mass% NaCl solution. The electrochemical measurements were conducted using a classical three-electrode electrochemical cell with a saturated calomel electrode (SCE) as the reference electrode, a platinum foil as the counter electrode, and the tinplate with an exposed area of 1 cm<sup>2</sup> as the working electrode. Before experiments, the tinplates were immersed into the solution for 1200 s until the open circuit potentials ( $E_{corr}$ ) became almost stable. The polarization curves were obtained by potentiodynamic scan starting from –500 mV (vs. SCE) more negative than  $E_{corr}$  (vs. SCE) to more positive potentials at a scanning rate of 1mV/s. EIS measurements were measured with the amplitude signal of 10 mV (peak to zero) at open circuit potential in the frequency range from 100 kHz to 0.1 Hz.

#### 2.3 Corrosion morphology observation

For the morphology observations after the electrochemical test, a scanning electron microscope (SEM, Inspect<sup>TM</sup> F, produced by FEI Company) was used for characterization.

#### **3. RESULTS AND DISCUSSION**





Figure 1 Corrosion potential of tinplate formed with different electrodeposition time in 3.5 mass% NaCl solution

Figure 1 shows  $E_{corr}$  evolution of the tinplate obtained at different electrodeposition time in 3.5 mass% NaCl solution as a function of immersion time. Clearly,  $E_{corr}$  for all the samples is not stable during the initial immersion time, and it tends to be stable as the immersion proceeds. Besides, the  $E_{corr}$  difference between each tinplate sample is not very dominant. Moreover, Figure 1 also shows that  $E_{corr}$  moves toward to a more positive direction as the electrodeposition time decreases from 120 s to 12 s,

indicating the great influence by electrodeposition time. Usually, the value of  $E_{corr}$  is not directly relevant to the corrosion rate, and it is more scientific to evaluate the corrosion resistance in terms of corrosion current density [16]. To further investigate the influence of electrodeposition time on corrosion evolution of tinplate, polarization curves and EIS have been employed to illustrate this.

#### 3.2 Influence of electrodeposition time on polarization curves evolution of tinplate in NaCl solution

Figure 2 shows the influence of electrodeposition time on polarization curves of tinplate in 3.5 mass% NaCl solution. All the tinplate samples show a very comparable polarization pattern. The cathodic branch corresponds to the reduction of dissolved oxygen. It is found that the corrosion current density slightly decreases with the electrodeposition time increasing from 12 s to 120 s. However,  $E_{corr}$  did not show a regular trend as the corrosion current density. Although the  $E_{corr}$  value moves toward to a more positive direction with the electrodeposition time decreasing from 120 s to 12 s, the corrosion current density increases gradually. The corrosion of metals in non-oxidizing solution usually displays patterns of uniform dissolution reaction in the anodic active region [17]: Sn $\rightarrow$ Sn<sup>2+</sup>+2e, oxygen reduction reaction in the cathodic region: 2H<sub>2</sub>O+O<sub>2</sub>+4e $\rightarrow$ 4OH<sup>-</sup>. For the corrosion of tinplate in non-oxidizing NaCl solution, the dissolved oxygen reduction is the dominant cathodic reaction. Of course, the structure and property of the tin coating layer can greatly affect the oxygen diffusion and reduction process. The intermetallic layer of FeSn<sub>2</sub> formed between the tin coating layer and base steel substrate plays a key role in the corrosion process, especially for tinplate with a lower coating mass. Therefore, the difference of  $E_{corr}$  of tinplate after different electrodeposition time is also related to the formation of intermetallic layer FeSn<sub>2</sub> on tinplate [1].



Figure 2 Potentiodynamic polarization curves of tinplate formed with different electrodeposition time in 3.5 mass% NaCl solution

Usually, the value of  $E_{corr}$  is not directly relevant to the corrosion rate. It is more scientific to evaluate the corrosion resistance in terms of corrosion current density [16]. Thus, the moderate corrosion current density increasing exhibits the intense attack characteristics of the sample obtained at 12 s

electrodeposition. The decreased corrosion current density with the increasing electrodeposition time can be attributed to the lower oxygen reduction rate on tinplate with a higher coating mass. Along with the decrease in electrodeposition time, the cathodic reduction rate of oxygen is enhanced. According to mixed potential theory [18],  $E_{corr}$  shifts to a more noble value with the increasing reaction rate of the oxidizing agent while corrosion rate is determined by charge-transfer processes. The variation of  $E_{corr}$  in the tinplate sample with electrodeposition time from 12 s to 120 s observed in the present work is explained by considering the above model. If the tin coating thickness through which metal ions diffusion increases with the coating mass increasing, and the decay in a local anodic current exceeds that for a local cathodic current,  $E_{corr}$  will certainly shift to a more noble value. Therefore, the corrosionpotential shift observed in the samples obtained at different electrodeposition time from 12 s to 120 s may due to the phenomenon described.



Figure 3 Visual observation of electrolyte color after potentiodynamic polarization curve measurements of tinplate formed with different electrodeposition time in 3.5 mass% NaCl solution. (a) 120 s; (b) 60 s; (c) 30 s; (d) 12 s

Figure 3 shows the visual observation of electrolyte color after polarization curve measurements of tinplate with different electrodeposition time in 3.5 mass% NaCl solution. Clearly, it can be seen from Figure 3(a) to Figure 3(d) that the electrolyte becomes more and more turbid as the electrodeposition time decreases from 120 s to 12 s, indicating and the most serious corrosion attack of tinplate obtained at 12 s electrodeposition time. Besides, the electrolyte color after the potentiodynamic polarization test is dark-green especially for the tinplate obtained at 12 s electrodeposition time in Figure 3(d). It may be inferred that the dark-green color lies in the presence of a large amount of Fe<sup>2+</sup> from the base steel after the perforation or corroding away of the tin coating on the tinplate [1]. For the tinplate obtained at 12 s electrodeposition time, the tin coating thickness is thin and the electrolyte can easily get through to corrode the base steel substrate, leading to a higher amount of Fe<sup>2+</sup> dissolution than the tinplate obtained at longer electrodeposition time with coating mass higher than 1.1 g·m<sup>-2</sup>. Therefore, it can be concluded from Figure 3 that the tinplate obtained at 12 s electrodeposition time suffers the most serious corrosion

attack among the four tested samples. To further illustrate this, corrosion morphologies of samples after potentiodynamic polarization tests have been observed.



**Figure 4** Corrosion morphology after potentiodynamic polarization curve measurements of tinplate formed with different electrodeposition time in 3.5 mass% NaCl solution. (a) 120 s; (b) 60 s; (c) 30 s; (d) 12 s

Figure 4 shows the corrosion morphology of tinplate obtained at different electrodeposition time with different coating mass after potentiodynamic polarization tests in 3.5 mass% NaCl solution. Figure 4(a) shows that the corrosion on tinplate at 120 s electrodeposition time with 11.2 g·m<sup>-2</sup> tin coating mass is not serious and the helco-like corroded area is mainly developed at special sites. Figure 4(b) shows that the tinplate at 60 s electrodeposition time with 5.6 g·m<sup>-2</sup> tin coating mass has a larger corrosion area than the sample in Figure 4(a). The corrosion pits on tinplate at 30 s electrodeposition time with 2.8 g·m<sup>-2</sup> tin coating mass have a larger depth as is shown in Figure 4(c). However, Figure 4(d) indicates that the tin coating on the sample at 12 s electrodeposition time with 1.1 g·m<sup>-2</sup> coating mass has been corrosion morphology result is in accordance with the visual observation of electrolyte color after polarization curve measurements in Figure 3. Besides, the large amount of Fe<sup>2+</sup> corroded from the base steel to electrolyte leads to the dark-green color visual observation of the electrolyte in Figure 3(d). Figure 4 also indicates that a lower coating mass of 1.1 g·m<sup>-2</sup> on tinplate at 12 s electrodeposition time

cannot provide enough protectiveness to base steel compared with other three higher coating mass samples obtained at longer electrodeposition time, i.e. the coating mass of  $1.1 \text{ g} \cdot \text{m}^{-2}$  on tinplate can greatly affect its corrosion protection ability to base steel. Therefore, the sample obtained at 12 s electrodeposition time with a tin coating mass of  $1.1 \text{ g} \cdot \text{m}^{-2}$  cannot provide enough corrosion protection effect to base steel substrate in the 3.5 mass% NaCl solution environment.

### 3.3 Influence of electrodeposition time on electrochemical impedance spectroscopy evolution of tinplate



**Figure 5** Electrochemical impedance spectroscopy of tinplate formed with different electrodeposition time in 3.5 mass% NaCl solution. (a) Nyquist plot; (b) and (c) Bode plots

Figure 5 shows the Nyquist impedance plots (Figure 5(a)) and Bode plots (Figure 5(b) and Figure 5(c)) for the tinplate samples obtained in 3.5 mass% NaCl solution as a function of electrodeposition time. Generally, the charge transfer resistance at the coating/steel interface dominates at low frequency, and the resistance of the tin coating dominates at high frequency as indicated by the fact that the phase angle closes to  $0^{\circ}$  [19]. Figure 5(b) shows that the impedance at the high frequency almost keeps the same and the impedance at the low frequency increases as the electrodeposition time increases from 12 s to 120 s, indicating the enhanced corrosion resistance of tinplate at 120 s electrodeposition time with a higher coating mass of 11.2 g·m<sup>-2</sup>. Figure 4(c) shows that the phase angle peak shifted to the low-frequency side as the electrodeposition time increase, indicating an increase in the impedance of the

tinplate [20]. Figure 4(c) also shows the fact that the low-frequency phase angle increases as the electrodeposition time increases due to the increasing resistance of the tinplate obtained at a longer electrodeposition time with a higher coating mass [21].



**Figure 6** The equivalent circuit used for fitting EIS results of tinplate formed with different electrodeposition time in 3.5 mass% NaCl solution.  $R_s$  – solution resistance;  $Q_m$  – tin coating capacitance;  $R_m$  – tin coating resistance;  $Q_{dl}$  – double layer capacitance;  $R_{ct}$  – charge transfer resistance

Accordingly, a general equivalent electrical circuit is proposed and depicted in Figure 6. Elements used in the equivalent circuit are as follows:  $R_s$  represents the electrolyte resistance;  $R_m$  and  $Q_m$  represent the resistance and capacitance of tin coating, respectively;  $R_{ct}$  represents the charge transfer resistance which is associated with both the anodic reaction and cathodic reaction, and  $Q_{dl}$  represents double layer capacitance. Table 2 shows the fitting results of the EIS data of tinplate obtained at different electrodeposition time with different coating mass in 3.5 mass% NaCl solution.

**Table 2.** Fitting results of the EIS data in 3.5 mass% NaCl solution of tinplate obtained at different electrodeposition time with different coating mass (in  $g \cdot cm^{-2}$ )

Electrodeposition	$Q_{ m m}(\Omega^{-1}\cdot$	$cm^{-2} \cdot s^{-n1}$ )	$R_{\rm m} \times 10^5$	$Q_{ m dl}(\Omega^{-1}\cdot$	$cm^{-2} \cdot s^{-ndl}$ )	$R_{\rm ct} \times 10^6$	$x^2 \times 10^{-4}$
time	<i>Y</i> <sub>0</sub> ×10 <sup>-6</sup>	$n_1$	$(\Omega \cdot cm^2)$	<i>Y</i> <sub>0</sub> ×10 <sup>-6</sup>	$n_{\rm dl}$	$(\Omega \cdot cm^2)$	
120 s	9.901	0.8347	9.068	5.643	0.8153	3.998	6.57
60 s	6.834	0.8807	7.902	4.908	0.9001	2.878	1.66
30 s	8.342	0.8488	6.892	3.546	0.8876	2.179	5.99
12 s	1.083	0.8035	4.722	2.291	0.9010	1.639	4.77

The standard deviations  $x^2$  were in the order of  $10^{-4}$ , and the relative error for each parameter was less than 10 %. For better understanding and illustrating, the calculated parameters  $R_m$  and  $R_{ct}$  for the tinplate samples are shown in Figure 7. Clearly, both  $R_m$  and  $R_{ct}$  in Figure 7 increase with increasing the electrodeposition time, indicating the enhanced corrosion resistance of the tinplate sample with an increased coating mass. The lower  $R_m$  and  $R_{ct}$  value of tinplate obtained at 12 s electrodeposition time

with a coating mass of  $1.1 \text{ g} \cdot \text{m}^{-2}$  may due to the poor boundaries to the base steel substrate, microcracks, residual porosity, and rough surface associated with the tinplate of  $1.1 \text{ g} \cdot \text{m}^{-2}$  tin coating mass obtained at 12 s electrodeposition time [22]. The evolution of  $R_{\text{m}}$  and  $R_{\text{ct}}$  reflects the changes in resistance of the tin coating, and the charge transfer resistance, respectively.  $R_{\text{m}}$  is closely related to the property of tin coating, such as porosity, adhesion to the base steel substrate, compactness, etc., and thus affects the variation of  $R_{\text{ct}}$  at the coating/substrate interface. Figure 7 also shows that for each sample  $R_{\text{ct}}$  is always lower than  $R_{\text{m}}$ , indicating that tin coating has better corrosion resistance than the base steel substrate. The increased  $R_{\text{m}}$  of tinplate sample as the electrodeposition time increases from 12 s to 120 s, indicates that a higher tin coating mass can contribute to enhanced corrosion resistance. At the same time, the increased  $R_{\text{ct}}$  as the electrodeposition time increases indicates that the corrosion electrolyte has increased difficulty in penetrating the tinplate with a higher coating mass. Therefore, the EIS results can reflect the tin coating structure and its corrosion evolution with the coating mass obtained at different electrodeposition time.



Figure 7 The evolution in parameters of  $R_m$  and  $R_{ct}$  obtained from EIS data of tinplate formed with different electrodeposition time in 3.5 mass% NaCl solution

Figure 8 shows the surface morphology of tinplate obtained at different electrodeposition time with different coating mass. Clearly, the commercially produced tinplate base steel surface is not very flat with a lower roughness. The sample obtained at 12 s electrodeposition time with a lower coating mass of  $1.1 \text{ g} \cdot \text{m}^{-2}$  in Figure 8(d) may not evenly distribute and cover the base steel surface, leaving the presence of obvious scratches or other defects. These defects facilitate the penetration of the corrosive electrolyte through the tin coating to the base steel substrate, leading to the lower  $R_{ct}$  for the tinplate sample obtained at 12 s electrodeposition time with  $1.1 \text{ g} \cdot \text{m}^{-2}$  coating mass. For the tinplate sample obtained at 120 s electrodeposition time with  $11.2 \text{ g} \cdot \text{m}^{-2}$  coating mass, the coating thickness is thick enough to cover the base steel surface defects, Figure 8(a), and therefore, it has the higher value of  $R_{m}$  and  $R_{ct}$  than the other three samples obtained at shorter electrodeposition time with lower coating mass. The sample obtained at 12 s electrodeposition time with a lower coating mass of  $1.1 \text{ g} \cdot \text{m}^{-2}$  cannot uniformly cover the base steel surface and facilitate the electrolyte transportation through thinner tin

coating layer to coating/steel interface leading to a higher corrosion tendency. Therefore, the amount of tin coating mass on tinplate can greatly affect its corrosion evolution behavior, and the tinplate sample obtained at 12 s electrodeposition time with a coating mass of 1.1  $g \cdot m^{-2}$  cannot provide corrosion protection effect to steel substrate in 3.5 mass% NaCl solution environment.



Figure 8 Surface morphology of tinplate formed with different electrodeposition time. (a) 120 s; (b) 60 s; (c) 30 s; (d) 12 s

#### 3.4 Corrosion mechanism discussion

It is acknowledged that the electrochemical cathodic and anodic reactions of tin in chloridecontaining solution are the reduction of oxygen and the dissolution of tin, respectively. The reduction of oxygen is given by Eq. (2), and the anodic dissolution of tin is quite complicated. Some possible anodic reactions were reported in the literature [17,23], including Eq. (3) to Eq. (7):

$2H_2O + O_2 + 4e = 4OH^-$	(2)
$Sn = Sn^{2+} + 2e$	(3)
$\mathrm{Sn}^{2+} + \mathrm{2OH}^{-} = \mathrm{Sn(OH)}_{2}$	(4)
$\mathrm{Sn}^{2+} + 2\mathrm{OH}^{-} = \mathrm{SnO} + \mathrm{H}_{2}\mathrm{O}$	(5)

$\mathrm{Sn(OH)}_2 + 2\mathrm{OH}^- = \mathrm{Sn(OH)}_4 + 2\mathrm{e}$	(6)
$\operatorname{SnO} + \operatorname{H}_{2}\operatorname{O} + 2\operatorname{OH}^{-} = \operatorname{Sn}(\operatorname{OH})_{4} + 2e$	(7)

Most of  $Sn(OH)_2$  and  $Sn(OH)_4$  will further dehydrate and change to more stable tin oxide (SnO and SnO<sub>2</sub>) as following reactions [24]:

$$Sn(OH)_{2} = SnO + H_{2}O$$

$$Sn(OH)_{4} = SnO_{2} + 2H_{2}O$$
(8)
(9)

With the presence of a large amount of corrosive Cl<sup>-</sup>, it tends to preferentially absorb on the special sites, such as defect lattice, scratches, or higher Sn containing area. These defects facilitate the penetration of the corrosive electrolyte through the tin coating to the base steel substrate, leading to the lower  $R_{ct}$  for the tinplate sample obtained at 12 s electrodeposition time with 1.1 g·m<sup>-2</sup> coating mass. For the tinplate sample obtained at 120 s electrodeposition time with 11.2 g·m<sup>-2</sup> coating mass, the coating thickness is thick enough to cover the base steel surface defects, and therefore, it has the higher value of  $R_m$  and  $R_{ct}$  than the other three samples lower coating mass. Besides, the lower coating mass of 1.1 g·m<sup>-2</sup> obtained at 12 s electrolyte transportation time cannot uniformly cover the base steel surface and facilitate the electrolyte transportation through thinner tin coating layer to coating/steel interface leading to a higher corrosion tendency, and the corrosion process will be accelerated. Moreover, the Cl<sup>-</sup> ions cannot be consumed out during the corrosion process [23]. The corrosion deterioration of the tinplate often occurs during longer storage and operation, and thus affects the subsequent processing property.

To sum up, a short electrodeposition time can lead to a lower tin coating mass with less coverage on the steel substrate surface and thus lead to the rapid loss of tin coating when exposing the tinplate to NaCl solution and premature failure can occur. Nowadays, although there is a need in reducing the tin amount (tin coating mass and distribution) used in the tinplate industry, a shorter electrodeposition time with poor tin coating quality on tinplate surface is not recommended, and besides the requirement for a flat and uniform steel substrate surface with a lower roughness should also be taken into consideration for better application of tinplate, especially with lower tin coating mass.

## 4. CONCLUSIONS

The influence of electrodeposition time on corrosion performance of tinplate in 3.5 mass% NaCl solution has been investigated by electrochemical measurements and SEM observations. The results indicate that the tinplate obtained at 120 s electrodeposition time with a higher tin coating mass of 11.2  $g \cdot m^{-2}$  exhibits much better corrosion resistance than the sample with lower tin coating mass obtained at 12 s electrodeposition time due to that a lower tin coating mass of 1.1  $g \cdot m^{-2}$  may not uniformly cover the base steel surface with roughness or other defects. Besides, the presence of a large amount of Cl<sup>-</sup> can greatly affect the corrosion behavior of tinplate with different coating mass obtained at different electrodeposition time. Therefore, the electrodeposition time of the tinplate can greatly affect its corrosion evolution behavior and a shorter electrodeposition time with a coating mass of 1.1  $g \cdot m^{-2}$  on the tinplate cannot provide corrosion protection effect to steel substrate in 3.5 mass% NaCl solution environment.

#### References

- 1. D. H. Xia, S. Z. Song and J. H. Wang, Trans. Nonferrous Met. Soc. China, 22 (2012) 717.
- 2. A. S. Tselesh, Thin Solid Films, 516 (2008) 6253.
- 3. L. S. Ren, Y. X. Hou and C. J. Li, Shandong Metall., 35 (2013) 10.
- 4. S. A. M Refaey and G. Schwitzgebel, Appl. Surf. Sci., 135 (1998) 243.
- 5. M. Jafarian, F. Global and I. Danaee, *Electrochim. Acta*, 53 (2008) 4528.
- 6. L. X. Hu, J. Cheng and W. Zhan, *Electroplat. Pollut. Control*, 29 (2009) 29.
- 7. W. Bo, Plat. Finish., 36 (2014) 25.
- 8. R. B. Chu, Z. X. Wang and S. C. Wu, Electroplat. Finish., 33 (2014) 57.
- 9. J. Sun, C. Q. An and Y. Tan, J. Mater. Eng., 3 (2010) 25.
- 10. N. Wint, S. Geary and H. N. McMurray, J. Electrochem. Soc., 162 (2015) C775.
- 11. H. Y. Ha, J. Y. Kang and J. Yang, Corros. Sci., 102 (2016) 355.
- 12. A. Arazna, A. Krolikowski and G. Koziol, Mater. Corros., 64 (2013) 914.
- 13. X. K. Zhong, G. A. Zhang and Y.B. Qiu, Corros. Sci., 66 (2013) 14.
- 14. D. H. Xia, S. Z. Song and J. H. Wang, Acta Phys. Chim. Sin., 28 (2012) 121.
- 15. F. J. Wu, X. J. Liu and X. Xiao, Int. J. Electrochem. Sci., 15 (2020) 8119
- 16. D. J. Zhou, J. H. Wang and Y. Gao, Int. J. Electrochem. Sci., 12 (2017) 943.
- 17. D. Li, P. P. Conway and C. Liu, Corros. Sci., 50 (2008) 995.
- 18. M. N. Wang, C. Qiao and X. L. Jiang, J. Mater. Sci. Technol., 51 (2020) 40.
- 19. C. Qiao, M. N. Wang and L. Hao, J. Mater. Sci. Technol., 75 (2021) 252.
- 20. F. Masfeld, S. Lin and Y.C. Chen, J. Electrochem. Soc., 135 (1988) 906.
- 21. A. A. Addi, E. A. Addi and I. Bakas, Int. J. Electrochem. Sci., 9 (2014) 8465.
- 22. F. J. Wu, X. J. Liu and X. Xiao, Surf. Eng., 34 (2018) 462.
- 23. C. Qiao, M. N. Wang and L. Hao, J. Alloys Compd., 852 (2021) 156953.
- 24. C. Lee, B. Nam and W. Choi, Mater. Lett., 65 (2011) 722.

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