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Corrosion Mechanism Differences of Tinplate in Aerated and Deaerated Citric Acid Solution

Yao Che[1], *Zhewen Han* [1], *Bing Luo*[2,3], *Dahai Xia*[1, *], *Jiangbo Shi* [1], *Zhiming Gao*[1], *Jihui Wang*[1,*]

[1] School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China;
[2] 94277 Unit of the Chinese People's Liberation Army, Ji'nan 250023, China;
[3] Automobile Engineering Department, Military Transportation University, Tianjin 300161, China
[*]E-mail: dahaixia@yeah.net; jhwang@tju.edu.cn

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The corrosion behavior of tinplate in 0.1mol/L citric acid solution in aerated and deaerated conditions, respectively, were studied by a combination of electrochemical impedance spectroscopy (EIS), inductively coupled plasma (ICP) and scanning electron microscopy (SEM). Differences between the corrosion mechanisms in the two cases were analyzed. Under aerated conditions, three stages were distinguished during the corrosion process: the corrosion of tin coating, the corrosion of the carbon steel and the detachment of the surface corrosion product. ICP results showed that the Sn content in the solution increased at the early stage and then basically remained stable, while the Fe content increased continuously up to 184ppm. Under deaerated conditions, the corrosion process of tinplate was dominated by the anodic dissolution of the tin coating, and ICP analysis showed that the changing trend of Sn content in the solution resembled that of the aerated case while the Fe content kept very low. The corrosion mechanisms under the two conditions were therefore proved different.

Keywords: Tinplate; Corrosion Mechanism; Citric acid; Deaerate condition

1. INTRODUCTION

Tinplate basically consists of a low-carbon thin sheet of steel coated with pure tin on both side. Although the increasing use of new alternative materials in canning industry, such as aluminium and chromates steel sheet, etc., tinplate is still used widely in more than 80% of cases because of its bright appearance, good corrosion resistance and formability[1, 2]. However, there are significant problems related to the use of tinplate cans in corrosive food products, such as corrosion failure, loss of seal integrity or discoloration problems [3-5]. In addition, other studies also indicated that high level of tin in food product may lead to food safety problem. Though its corrosion products neither involve toxic substances nor influence flavor, very large doses can cause serious digestive disturbances[2, 4].

As we know, citric acid is naturally present in canned food and may participate directly in the electrochemical corrosion and/or passivation of the metal. Numerous studies have been focused on the electrochemical behavior of a tin electrode in citric acid solution. C. A. Gervasi et al.[6] utilized chronopotentiometry combined with impedance measurements to study the structure and composition of the anodic film formed on tin in citrate buffer and obtain properties of the anodic film itself. M. Jafarian et al.[7] studied pitting corrosion of tin in citric acid solution. Potentiostatic measurements showed that the overall anodic processes can be described by three stages. The first stage corresponds to the nucleation and growth of a passive oxide layer. The second involves pit nucleation and growth and the third stage involves repassivation. However, very few studies on the corrosion behaviors of tinplate exposed to citric acid solution have been reported, the corrosion behaviors in acid media are still uncertain. The corrosion process of tinplate is complex due to its stratified structure and heterogeneity. To be really protective, tin is advantageous to be anodic and show an electrochemical protective effect on carbon steel substrate [8, 9]. However, because the electronegativity of tin and steel is close, tin coupled with steel may even behave as the cathode if contacted with canned food containing species displaying so high activity towards iron ions or condition of tinned containers changes because of air leakage or deformation [10, 11]. I. A.Ammar et al.[12] reported that the corrosion behavior of tinplate in stagnant deaerated solutions of citric. In 0.1mol/L citric acids at pH 2-5, steel was found to be cathodic with rspect to Sn. In 0.3 mol/L citric acids at pH 5-6, Sn was initially anodic with respect to steel. However, reversal of polarity occurred after some time and steel became the anode of the couple. R. Toniolo et al.[13] studied metal release from tinned containers into preserved vegetables. Under different pH conditions and ligand Sn and Fe showed different polarity, which was strictly related to their starting oxidation potentials and their mutual position in these solutions. To our knowledge, little literature has paid attention to different protection character of tin layer and corrosion behaviors of tinplate between air and anaerobic conditions in citric acid solution. Given the special requirements of packing media of food, it is more reasonable and meaningful to study the corrosion behavior of tinplate in deaerated condition [14, 15].

The present work studied the corrosion mechanism and process of tinplate in 0.1mol/L citric acid during natural immersion in aerated and deaerated conditions, using a combination of EIS with SEM and ICP. Electrochemical parameters, cross section morphology and metal release can be used to analyze the formation and detachment of corrosion product film, the dissolution of tin coating/carbon steel matrix in citric acid.

2. EXPERIMENTAL

2.1 Materials

The tinplate sheets were provided by the ORG Canmaking Company. The thickness of the tin coating on both sides was about 3μm. The samples(70mm[L]×70mm[W])were degreased with ethanol, and then dried before electrochemical measurement.

2.2 Electrochemical measurements

The potentiodynamic polarization and EIS measurements were carried out in a self-made electrolytic cell using a VersaSTAT 4 electrochemical workstation (Princeton Applied research, USA) and VersaStudio control software. The potentiodynamic polarization experiments were performed at a scan rate of 0.1667mV/s. EIS measurements were performed at the open-circuit potential with a 5 mV amplitude signal and the applied frequency ranged from 100 kHz to 0.01 Hz. A three-electrode cell with the tinplate as the working electrode (WE), a antimony electrode as the reference electrode (RE) and a commercial ruthenium-titanium electrode as the counter electrode (CE) was used. The samples were tested in two different conditions: (Ⅰ) in aerated condition (Ⅱ) in deaerated condition. In the later condition, the hermetic experimental device was vacuumized by a vacuum pump and filling N_2 until air was taken out entirely before testing. The sample were exposed to 0.1mol/L citric acid solution at room temperature (25±2℃) and examined periodically by EIS technique. The data acquired by ZSimpWin Software.

2.3 Morphology and Microstructure Analysis

Samples were cut out and embed in epoxy resin vertically, cross-section images were obtained with a field-emission scanning electron microscope (FE-SEM S4800; Hitachi, Japan).

2.4 Elements Analysis

During immersion, the concentrations of dissolved metals (Sn and Fe) in electrolyte were detected by inductively coupled plasma periodically (ICP). ICP measurements of microwave digested samples were performed by a Spectromass Type VISTA-MPX.

3. RESULTS AND DISCUSSION

3.1 Electrochemical impedance

3.1.1 In aerated citric acid solution

The impedance spectra measured for tinplate in aerated 0.1mol/L citric acid solution with typical immersion time are shown in Fig. 1.

At the first day, the general shape of the spectra includes impedance response of a corrosion process at higher frequencies and an obvious transfer process at lower frequencies (Fig. 1(a)). With increasing immersion time, the Warburg tail disappeared and the Bode plot showed a characteristic with two time constants (Fig. 1(b') and (c')), indicating that the electrolyte had permeated through the defects of the tin coating and double layer capacitance was formed on the substrate metal interface. The time constant observed at higher frequency region was attributed to the charge transfer reaction in the tin coating, the time constant at lower frequency was attributed to the charge transfer reaction in the electric double layer formed at the interface between coating and substrate. The value of | Z| decreased remarkably to $10^3\Omega\cdot cm^2$ (Fig. 1(c')).

To analyze the EIS spectra of tinplate in aerated solution, equivalent electrical circuit models shown in Fig. 2 were used.

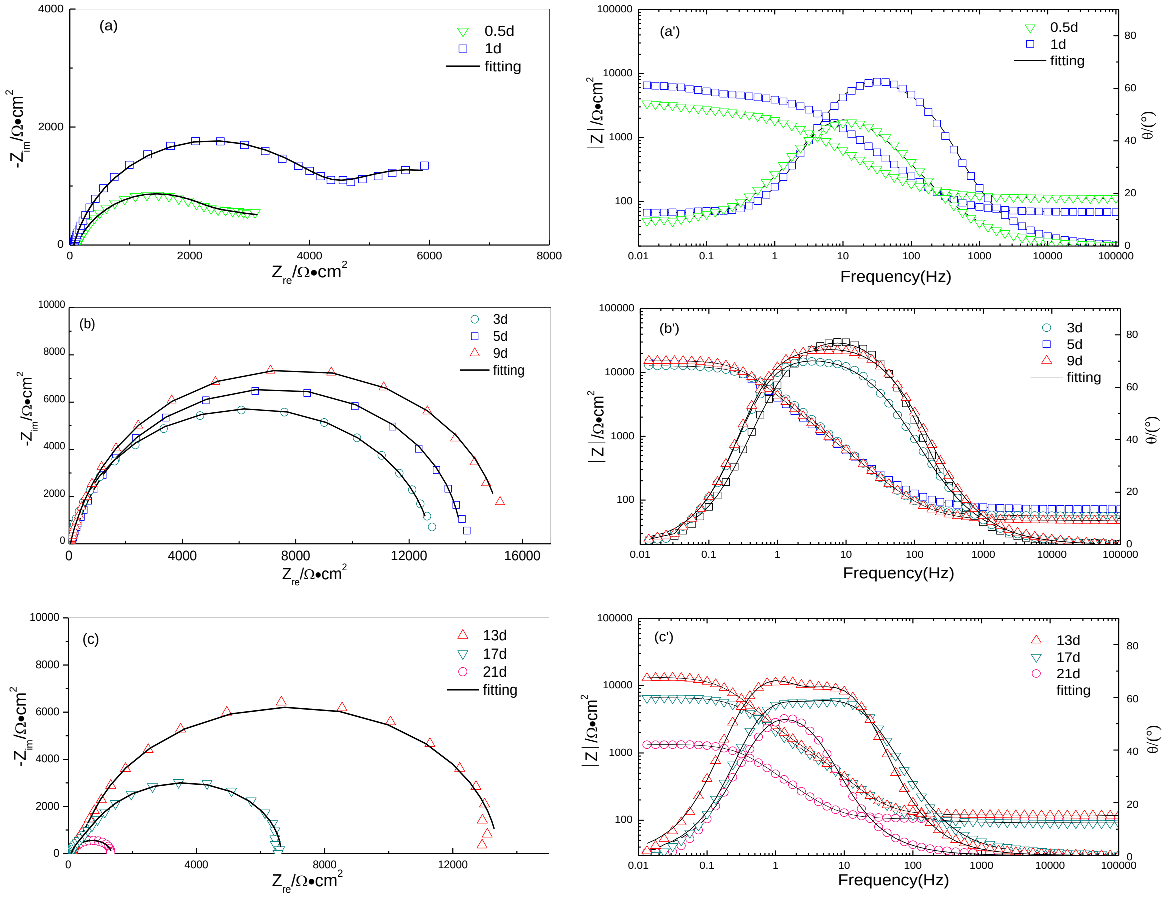


Figure 1. EIS plots of Tinplate exposed to 0.1 mol/L citric acid solution in the aerated condition for different days

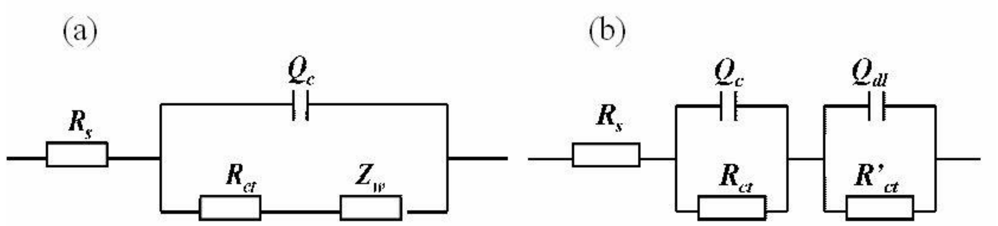


Figure 2. Electrochemical equivalent circuits for tinplate in 0.1 mol/L aerated and deaerated citric acid solution, R_s is the electrolyte resistance, Q_c is the tin coating interface capacitance, R_{ct} is the charge transfer resistance of tin coating, R'_{ct} is the charge transfer resistance of substrate, Q_{dl} is the double layer capacitance and Z_w is the Warburg resistance. (a) one time constant with Warburg tail circuit,;(b) two time constants circuit

The R_{ct} and R'_{ct} values obtained from the electrochemical equivalent circuit are shown in Fig. 4. The R_{ct} increased sharply during the early days immersion, then the curve kept nearly stable followed by a smooth decrease. These changes could be due to not only the contact resistance of metal but also the protective layer from the insoluble corrosion products. Formation and deposition of insoluble corrosion products blocked the tiny pore channel in tin coating and suppressed the diffusion of corrosive species effectively as a barrier layer, so the R_{ct} increased sharply at the beginning of the immersion period. Then the insoluble corrosion products would be destroyed or came off and more corrosion ions arrived at the interface of tinplate, so R_{ct} dropped at the later period of the immersion. The R'_{ct} kept nearly stable value during 5-10 days immersion and then decreased, which indicated that the corrosion on carbon steel substrate became more and more serious. With increasing immersion time, the penetration of water and movement of ionic species through the coating layer increased the coating conductivity, so the resistance decreased.

3.1.2 *In deaerated citric acid solution*

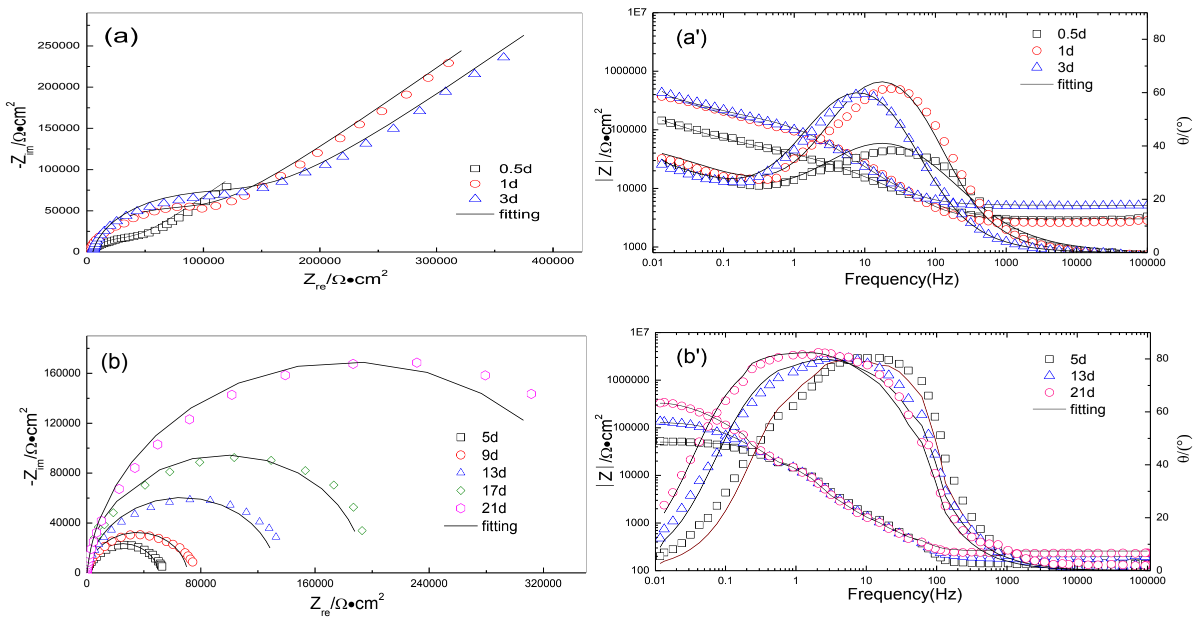


Figure 3. Nyquist and Bode plots of Tinplate exposed to 0.1 mol/L citric acid solution in anaerobic condition for different days

In Fig.3, the EIS diagrams are presented of tinplate in 0.1mol/L deaerated citric acid solution for different immersion times which are quite different to that in aerated solution. At the beginning of the immersion period (Fig. 3(a)), the high frequency semicircle generally corresponds to the properties of the tin coating, while the lower frequency a typical Warburg impedance character gave information about the corrosion reaction in the tin coating which was controlled by diffusion process or the mix of charge-transfer and the diffusion process. With increasing immersion time, one capacitive loop was shown in Nyquist plots (Fig. 3(b)). The radius of capacitance arc increased and an enhanced corrosion resistance was presented in Bode plots with an increased |Z| value (Fig. 3(a') and Fig. 3(b')). Finally the value of |Z| increased remarkably to $10^4\Omega\cdot cm^2$.

The impedance spectra were simulated with the electrochemical equivalent circuits (Fig. 2(a)). The R_{ct} reflected charge transfer resistance of metal surface and the values are shown in Fig. 4. Because of the accumulation of corrosion product at the surface of tinplate all the time, the R_{ct} value increased by 2 orders of magnitude during immersion, from 12200 Ω•cm^2 to 266600 Ω•cm^2. The R_{ct} is inversely proportional to corrosion rate, so the increase of R_{ct} indicated that influence of corrosion product restrained corrosion reaction at surface of tinplate.

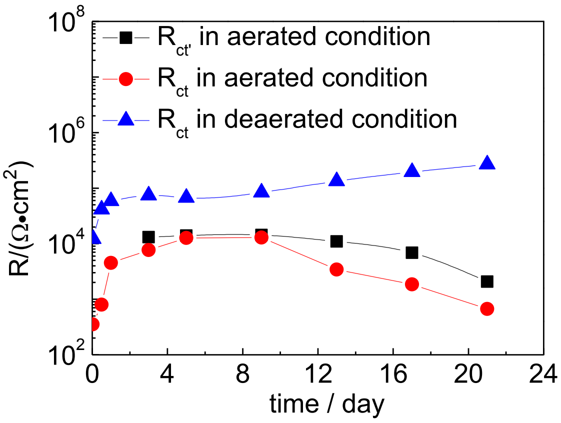


Figure 4. Fitting results of Electrical equivalent circuit

3.2 Morphology and composition

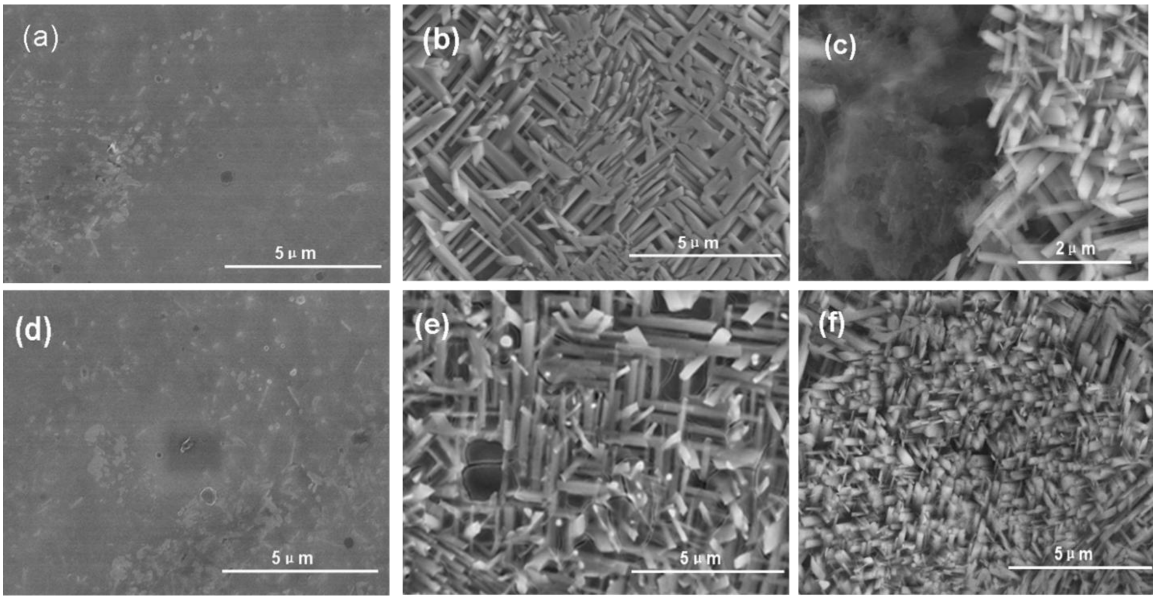


Figure 5. SEM surface images of tinplate before(a,d) and after exposed to 0.1mol/L citric acid solution for 9days(b,e) and 20 days(c,f)

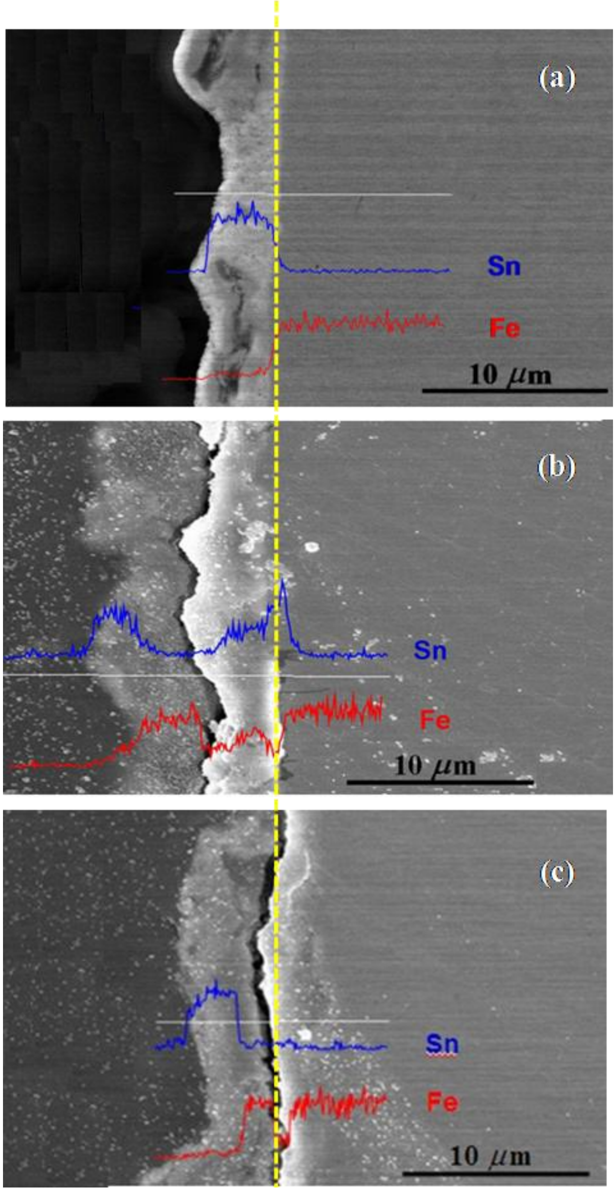


Figure 6. Compositional line profiles of the cross section images, which were probed by EDS spectroscopy scanning along the white line: (a) before exposure ;(b) after exposure in aerated condition; (c) after exposure in deaerated condition to 0.1 mol/L citric acid solution for 20 days

In deaerated contition, large amount of stick-shaped corrosion products that covered the whole surface could be observed on the sample surface after immersion for 20 days in deaerated citric solution (Fig. 5(f)).

Fig. 6 is the cross section morphology and compositional line profiles of tinplate before and after exposure to 0.1 mol/L citric acid solution for 20 days. The compositional line profiles were probed by energy-dispersive X-ray spectroscopy (EDS), main exhibiting Fe and Sn signals across the cross section. As shown in Fig. 6(a), tinplate is made of low-carbon steel sheet coated with pure tin coating about 3μm as mentioned above. As shown in Fig. 6(b) , there was a corrosion products film formed on the surface of tinplate after immersion for 20 days in aerated solution, which consists of a layered structure with outer Sn and inside Fe. Although the tin coating got thinner and the Sn content was less much than before immersion, it was still existed on carbon steel substrate. It is remarkable that both carbon steel substrate and tin coating were corroded by citric acid solution during immersion. In Fig. 6(c), the compositional line profiles for 20 days immersion was showed in deaerated solution. A layered corrosion products film can be also observed depositing on surface of tinplate, while Sn content is more than that in the air. The original tin coating almost cannot be observed, which indicated that tin coating was destroyed in deaerated condition by citric acid solution during immersion.

3.3 ICP results

The increase with time displayed by Fe and Sn release in 0.1 mol/L citric acid solution was shown in Fig. 7. As shown in Fig. 7(a), during immersion in deaerated solution, Sn release increased sharply during the early day's immersion, and then changed slowly. While Fe release was stable during whole immersion period, just a small increase was found at last days. Obviously, Fe release in 0.1 mol/L deaerated citric acid solution was much lower than Sn release, which may indicated that the tin coating was corroded seriously while carbon steel substrate was protected. Fig. 7(b) showed during immersion Fe and Sn release in aerated solution, in which Sn release kept nearly stable value while Fe release increased sharply after three day immersion. Contrary to in deaerated solution, it was found that a release of Fe was higher than that of Sn. The ionic dissolution were directly related with the corrosion on tin coating and carbon steel substrate, the results showed that the tin coating was preferential to dissolve in 0.1 mol/L aerated citric acid solution, but the corrosion of carbon steel substrate was much worse than the tin coating.

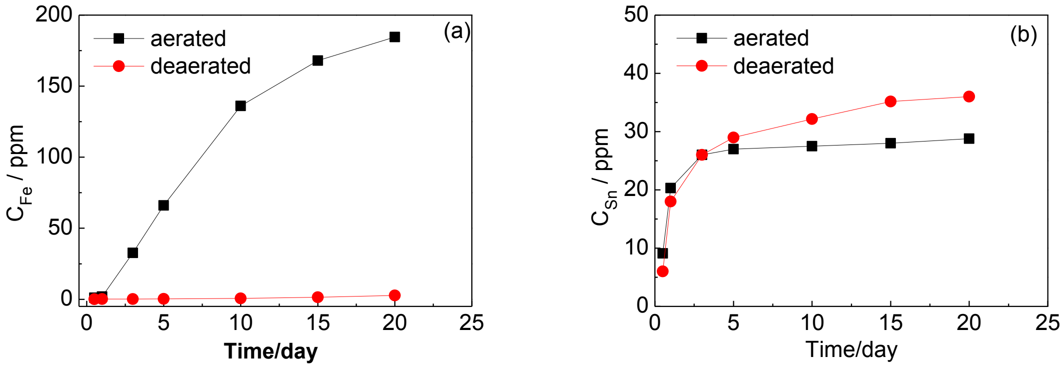
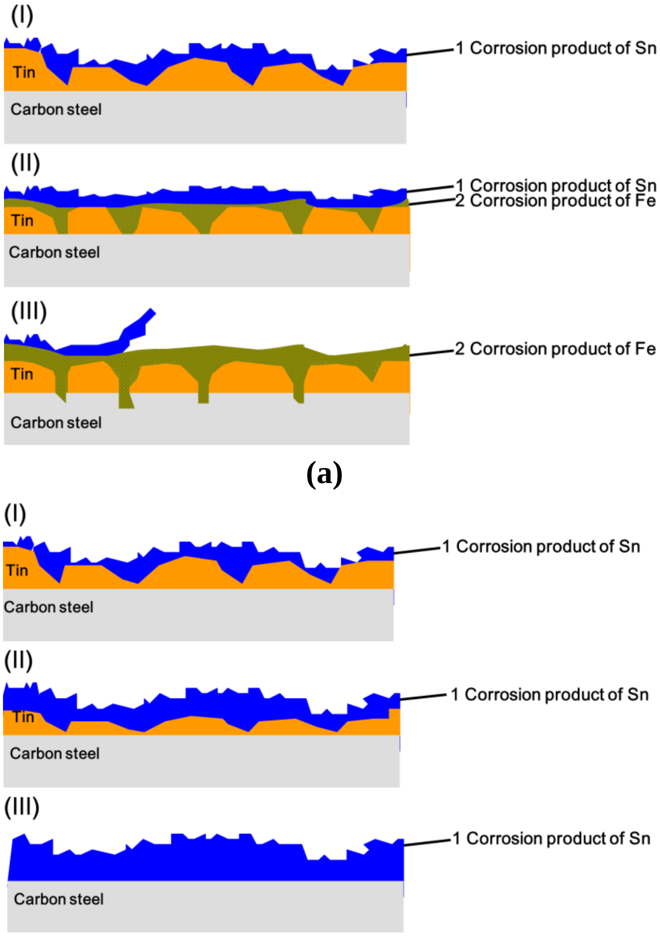


Figure 7. Fe and Sn release of tinplate exposed to 0.1mol/L citric acid solution for 20 days (a) Fe ; (b) Sn

3.4 Discussion

Therefore, with the help of EIS study of tinplate in 0.1 mol/L citric acid solution and SEM, ICP analysis above, some features and differences related with tinplate in 0.1 mol/L aerated and deaerated citric acid solution can be demonstrated in Fig.8 (a) and (b).



(a)

(b)

Figure 8. Schematic diagrams of the corrosion mechanism of tinplate (a) in aerated condition; (b) in deaerated condition

Both in aerated and deaerated citric acid solution, the R_{ct} increased sharply during the early days immersion, which is different from some other coating/metal systems, usually having a decreased R with the immersion time. This may result from accumulation of insoluble corrosion products which could seal the pore channels of the tin coating, further inhibiting the diffusion of the corrosive species and impeding ionic movement in the coating layer. This phenomenon was similar to that reported in the reference [3]. In reference [3], the authors investigated the corrosion mechanism of tinplate in functional beverage and found that an increase in the impedance modulus at low frequency was due to the corrosion product forming on the surface of the tinplate over the first 31 h. With an increase in the immersion time, a decrease in the impedance modulus at low frequency was due to the detachment of the corrosion product and the corrosion of the carbon steel substrate.

The immersed tinplate in aerated and deaerated citric acid solution showed different characters of corrosion. In aerated solution, at the beginning of the immersion period, tin coating was corroded by citric acid solution. With increasing immersion time, due to the potential difference between tin/carbon steel substrate and the weak complexation of Sn in aerated solution, corrosion occurred at exposed carbon steel substrate of tinplate where tin coating was corroded by aggressive solution and existed defects. At last immersion period, because the coating/substrate interface was destroyed by aggressive solution the corrosion products film and tin coating came off from the surface in some area. So in aerated citric acid solution steel is anodic to tin coating, the superficial Sn layer in tinplate acts only as a mere outward protective layer for the steel underlayer. In deaerated citric acid solution, the dissolution of tin coating was dominant during whole process of immersion. The corrosion behavior in this condition was determined by both the complexing strength of the acid anion and the kinetics of inhibition of the cathodic reaction. Fe was the nobler electrode of the couple, so tin is anodic to steel and tin coating showed an electrochemical protective effect on carbon steel substrate.

4. CONCLUSIONS

(1) EIS combined with SEM and ICP observations as discrimination indicators of a tinplate corrosion process were presented: In aerated citric acid solution, the shape of EIS spectra showed a characteristic with two time constants three days later. Fe release in solution was dominant; the tin coating was not seriously corroded while the carbon steel substrate corroded continuously. While in deaerated citric acid solution, the EIS spectra showed one capacitive loop characteristic during whole process. Fe release in solution was much lower than Sn, the tin coating was corroded seriously and cannot be observed in the SEM image.

(2) Due to the potential difference between tin and carbon steel in 0.1 mol/L citric acid solution, in aerated solution, steel is anodic to tin coating, the superficial Sn layer in tinplate acts only as a mere outward protective layer for the steel underlayer; in deaerated solution, tin is anodic, so that tin coating showed an electrochemical protective effect on carbon steel substrate.

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