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Electrochemical Synthesis of Phenol-aniline Copolymerization Coating on 304 Stainless Steel Anodes and Coating Microstructure Analysis

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Electrochemical copolymerization of phenol and aniline was achieved on 304 stainless steel anodes in neutral water solution with an electrolyte of Na₂SO₄. Compared with pit corrosion potential of different copolymer coatings, the best solution composition was 0.09 mol/L phenol and 0.01 mol/L aniline. Through infrared spectrum analysis, polyaniline structure was proved in phenol-aniline copolymer, as well as more side chains. Scanning electron microscope was used to analyze microstructure of copolymer coating, taking advantage of part solubility of phenol-aniline copolymer in tetrahydrofuran, the bifurcate network structure was observed. The copolymer coating microstructure was summarized, compared with the performance of polyphenol coatings, the reasons of corrosion resistance enhancement with the addition of aniline in electropolymerization reaction was assumed as well.

Key words: Electropolymerization, Phenol, Aniline, 304 stainless steel, Pit corrosion

I. INTRODUCTION

Electrochemical polymerization reactions have been studied for decades [1−7], and several organic compounds, such as aniline, phenol, thiophene, pyrrole, could be electropolymerized. Electrochemical polymerization of phenolic compounds was originally mentioned by McKinney et al. [8], and the molecular structure of polyphenol was \( (C_6H_4O)_n \).

Early research of phenol polymerization focused on the corrosion protection function of polyphenol coating for metal bases. In the patent published by Borman from General Electric [9], the electrochemical oxidation and polymerization occurred on surface of metal anodes, on which the polyphenol coating product showed fine corrosion resistance. The corrosion resistance property of polyphenol has been studied for many years [5, 10−13], but the application of polyphenol was limited because of the extensive use of organic solvent. In the process of phenol wastewater treatment, polyphenol was observed on catalytic anodes. These phenomena made researchers begin to study the electropolymerization of phenol in aqueous solution [14−18], which offered the possibility of the synthesis of electrochemical polyphenol coating in water solution instead of organic solvent [19, 20].

In previous research, aliphatic amine was often used in electropolymerization of phenol, in order to form thicker coating and better corrosion resistance [21, 22]. The absorption of amine on anode surface forced the polyphenol molecular growing perpendicular to the anode surface, otherwise it might grow attaching to electrode. However, aniline has still not been concerned. There were several advantages for adding aniline into the reaction of electrochemical polymerization of phenol. Firstly, the competitive adsorption of aniline performed just like the function of aliphatic amines. Secondly, aniline could also be electrochemical polymerized and form polyaniline, and aniline might be copolymerized with phenol under right electrochemical condition. Thirdly, the polyaniline coating on electrode was also corrosion resistant, so the corrosion resistant performance of phenol-aniline polymer coating could be improved.

In our former report [23], a polyphenol coating was generated on the surface of 304 stainless steel anodes by anodic oxidation. The microstructure of the polyphenol coating was analyzed, taking advantage of half dissolution of polyphenol in tetrahydrofuran. Polyphenol coating was composed of small polymer flakes with a diameter of 50 nm, so the weak connection between flakes led cracks appearing easily on the coating. The electrochemical polymerization mechanism of phenol has already been summarized [23]. The main process of polyphenol generation was about that the generation, transformation and coupling of phenolic radicals, follow with the polyphenol growth.

Polyaniline, widely used in the field of fuel cells, has been studied in metal corrosion protection for a long time [24]. The molecular structure, polymerization process, coating microstructure and performance

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of polyphenol and polyaniline were summarized. The molecular structures of polyaniline included reduction state, \((C_6H_4NH)_n\), and oxidation date, \((C_6H_4N)_n\). The molecular structure and aniline polymer were similar to polyphenol. The processes of aniline electropolymerization were studied by Genies and Tsintavis originally [25] and other researchers reported the mechanism of aniline electropolymerization [26, 27], shown in Fig.1, in which Eq.(5) was the anode reaction.

The polyaniline film microstructure had been reported exhaustively, Okamoto et al. described one film-forming mode of electrochemical polymerization of aniline [28, 29]. Polyaniline grew as the shape of long curves with lots of branches, vertical to the electrode base, then polyaniline curves were tangled each other and formed coating. The formation of polyaniline curve in electrochemical polymerization was helpful to connect polyphenol flakes closely and reform the polymer coating.

Aniline, oxidized on anode with the effects of hydrogen ions, formed aniline cation radicals as reaction (1) in Fig.1. The aniline cation radicals had three possible states shown in Fig.2 (d), (e), and (f). There was some similarity in the processes of phenol and aniline electropolymerization, the polymer growth came from the coupling of radicals, which were generated on anode surface during the electrochemical polymerization. The phenolic radicals in phenol polymerization also had three different states, shown in Fig.2 (a), (b), and (c). The coating of polyaniline was generated on 304 stainless steel surface through the cyclic voltammetry below the electrode potential of 1 V (vs. SCE) [27], and SCE (saturated calomel electrode) is the reference electrode. The phenol electropolymerization was carried out at the electrode potential of 1.45 V [23], higher than electropolymerization of aniline. It was possible to generate phenolic radicals and aniline cation radicals on anode surface at the same time, and achieve phenol-aniline electrochemical copolymerization, so the polymer coating could be further reformed.

In our research, for improving the microstructure of polyphenol coating, aniline was added into the electropolymerization reactions on 304 stainless steel anodes to bond polyphenol flakes and layers together, reduce the cracks in polyphenol coating and make the polymer coating become an entirety. The reactions of aniline and phenol electrochemical polymerization were compared. The corrosion resistance was contrasted among the electrochemical polymer coatings, synthesized with and without aniline, and the proper proportion of aniline was discussed according to the corrosion protection function. The chemical constitution of polymer coating was analyzed by infrared spectroscopy (IR) to study phenol-aniline electrochemical copolymerization. The microstructure of polymer coating, synthesized under proper phenol-aniline proportion, was studied by scanning electron microscope (SEM) taking advantage of half dissolution of polyphenol in tetrahydrofuran (THF) [23] to explain the change of corrosion resistance.

II. EXPERIMENTS

A. Synthesis of electrochemical polymer coating

304 stainless steel anodes were used in the electrochemical polymerization of phenol and aniline. All chemicals used were analytically pure and purchased from Beijing Chemical Factory (China). Water used in the experiments was distilled. The electrolytic bath was a 100 mL flask. Electrochemical tests were carried out on a CS300 electrochemical workstation. A three-electrode system was chosen in which the auxiliary electrode was platinum, the reference electrode was a SCE. The working electrode was a square of stainless steel with a side length of 10 mm and the other faces covered with insulating ethoxyline resin. The working electrode was shined with emery paper, washed by distilled water, and deoiled with ethanol before use. All electrochemical tests used SCE as the reference electrode. The 304 stainless steel electrodes was used as the anode and processed for 1 h in a neutral electrolyte at
an anodic potential of 1.45 V and a cell voltage of 2.5 V. The conducting medium was 0.1 mol/L Na$_2$SO$_4$. After the polymer coating on the stainless steel electrode became yellowish-brown, the covered electrode was used in other experiments.

**B. Measurement of pitting corrosion potential**

The coated stainless steel electrodes were dipped in 3.5% NaCl solution for 0.5 h until the open circuit potential kept stable and the stable open circuit potential was recorded. With the nitrogen blasting into the solution, at the scanning rate of 20 mV/min, the linear scanning was carried out, and the electrode potentials at the currents of 10 and 100 µA were recorded, in which the larger electrode potential were used as pitting corrosion potential. The pitting corrosion potentials of coatings generated at different phenol-aniline proportion were analyzed and compared to choose the proper phenol-aniline proportion in electropolymorization.

**C. Analysis of electrochemical polymer coating**

The electrochemical polymer coating deposited on the stainless steel electrode was collected and analyzed by a FTIR Spectrometer20 (Nicolet Corp.). The stainless steel electrode covered with the polymer coating was cleaned with distilled water, the surface topography of the coating was tested by a HITACHI S-4700 SEM. Soluble polyphenol was removed with tetrahydrofuran, and the microstructure of the cleaned coating was tested by SEM. The micrographs were used to study electrochemical phenol-aniline copolymerization coating formation and microstructure on the stainless steel electrode, explain the corrosion resistance change of polymer coating in NaCl solution.

**III. RESULTS AND DISCUSSION**

**A. Comparison of phenol and aniline electrochemical polymerization**

1. **Linear scanning test in phenol solution and aniline solution**

The electrochemical polymerization of phenol, which occurred on stainless steel electrode surface, led the synthesis of polymer coating that could change the surface properties of anodes, and the electropolymerization reaction was observed in linear scanning test. Figure 3(a) was the anodic polarization curve of 304 stainless steel in 0.1 mol/L Na$_2$SO$_4$ (the current $I$ and the anode potential $E$). In Fig.3(a), the current rose when the electrode potential reached 1.15 V and a current extremum was detected at 1.33 V. Then the current kept rising with the anode potential until the current maximum of 1 mA was achieved at 1.44 V. With the comparison of Fig.3 (a) and (b), the appearance of current maximum was the polymerization current when the polyphenol coating was forming on stainless steel electrode, and after the scanning a yellow brown smooth adherent polyphenol coating was synthesized on anode surface. After the current maximum, because the polyphenol coating generation blocked the oxidation and electron losing of phenol on anode surface, the anodic current decreased with the electrode potential increasing. The coating formation also blocked the oxygen evolution, so the current stayed low until the electrode potential reached 1.53 V, after which the current increased sharply with oxygen rapidly generating.

For Fig.3(c), at the beginning of the scanning, the current stayed low as same as Fig.3 (a) and (b). When the electrode potential reached 0.94 V, a current extremum was observed, then the current decreased quickly close to Fig.3 (a) and (b). As described by other researchers [24], the current peak should be the results of the generation of polyaniline that was shown as the product of Eq.(5) in Fig.1. Once the electrode potential reached 1.18 V, anodic current rose sharply again, and the maximum current of 2.6 mA was observed at the electrode potential of 1.27 V, while the product of polyaniline was synthesized quickly on anode surface. Then the current decreased as the electrode potential increased until the beginning of oxygen evolution at the electrode potential of 1.4 V. After the scanning, an invisible green polyaniline coating was observed on stainless steel surface. The synthesis of polyaniline coating made the oxygen evolution potential rise from 1.25 V to 1.4 V, but the oxygen evolution potential was still lower than the oxygen evolution potential, 1.53 V, in phenol solution. Under the same electrochemical condition, it was supposed that the corrosion protection and the integrity of polyaniline coating was both worse than polyphenol coating, because of the lower oxygen evolution potential of polyaniline coating shown in test, which meant easier oxygen generation and coating exfoliation. The better conductivity of polyaniline might be responsible for the phenomenon. From the comparison of the linear scanning curves, it
was realized that the polyphenol electrochemical synthesis had a relatively high reaction rate at the electrode potential of 1.44 V, and the polyaniline was synthesized more quickly at 0.94 and 1.27 V. So it seemed that aniline electropolymerization occurred more easily than phenol electropolymorization, it also meant aniline would be electropolymerized at the electrochemical reaction condition for polyphenol coating synthesis.

2. Cyclic voltammetry in phenol solution and aniline solution

Figure 4(a) was the cyclic voltammetry curve in 0.1 mol/L phenol at a scanning rate of 50 mV/s, in the electrode potential range of 0 and 1.5 V, for five scanning cycles. At the first cycle, it could be observed that a current extremum appeared at 1.38 V, then the current maximum of 1 mA was achieved at the electrode potential of 1.45 V. During the following cycles, the current peak could not be detected, a step-like peak at 1.43 V was observed instead. From the cyclic voltammetry, it was made sure that the phenol electropolymorization was an irreversible reaction, and the following polymerization was influenced by the coating forming in first cycle. Therefore, from the second cycle the current peak did not appear again. However, the electropolymorization still occurred, the anodic current at 1.43 V became step-like and weaker as the cycle number increased.

For Fig.4(b), in first cycle included a smaller current extremum at 0.93 V and the current maximum at the electrode potential of 1.28 V, as the same current variation as it showed in the linear scanning curve. The cathodic scanning began when the electrode potential reached the oxygen evolution potential. During cathodic scanning, there was not any notable cathodic extremum observed, so electropolymorization of aniline on stainless steel was an irreversible reaction. The difference between phenol and aniline polymerization was that during the following 4 cycles in aniline solution the anodic current maximum did not appear, and the anodic and cathodic scanning curves almost overlapped. After 5 cycles, the polyaniline coating on stainless steel surface was still thin and the electrode base was still visible. According to the literature [24], notable reductive current maximum could be detected in the cyclic voltammetry test of aniline on stainless steel electrode when the scanning potential range was kept below 1 V. This phenomenon was not observed in our tests, because the reductive current, which came from the transformation of polyaniline shown as Eq.(6) in Fig.1, was much weaker than the oxidative current maximum at 1.28 V, which meant a much higher electropolymorization reaction rate.

The fact that the generation potential of polyaniline was lower than the generation potential of polyphenol was observed in the cyclic voltammetry tests, the same conclusion with the linear scanning tests. Besides, the external appearance and the formation processes of polyphenol and polyaniline coatings, which were synthesized in the same reaction condition, had significant difference. During the first scanning cycle, polyaniline was generated for a large amount as the appearance of current maximum, which meant a larger generation rate than polyphenol. However, during the following cycles, the oxidative current in polyaniline generation was much lower than in polyphenol generation, which caused the thinner coating of polyaniline. In a word, at 1.43 V, the polyaniline coating formation might disturb the continuous aniline electropolymorization, but the polyphenol could be generated on the former polyphenol coating, though the impeditive effects of the polyaniline coating for polymerization also existed.

From the results of linear scanning and cyclic voltammetry, the current maximum of phenol polymerization on 304 stainless steel electrodes was observed during the potential range of 1.4−1.45 V, so the potential range was the most propitious to the polyphenol coating formation. Further, more, the aniline could also be polymerized at the same potential range in some degree, which provided the possibility for phenol-aniline copolymerization on stainless steel. So during the electropolymorization, a potentiostatic method with the electrode potential of 1.45 V and the reaction time of 1 h was chosen for the synthesis of polyphenol, polyaniline, phenol-aniline copolymer coating, while the bath voltage was about 2.5 V. After the coating formation, the stainless
steel anodes were used to check the corrosion resistance, while the chemical constitution and the microstructure of polymer coating were also studied.

B. Comparison of corrosion resistance of polyphenol and polyaniline coating in NaCl solution

In order to compare the protection effects of polyphenol coating and polyaniline coating on stainless steel, some linear scanning experiments were carried out on naked, polyaniline coated and polyphenol coated stainless steel anodes. The linear scanning curves were shown in Fig.5. The polyphenol coating and polyaniline coating were synthesized separately in 0.1 mol/L phenol solution and 0.1 mol/L aniline solution at the same electrochemical condition. When the anodic current came to 1 mA, the scanning was stopped automatically to protect the stainless steel from serious pitting corrosion.

3.5% NaCl medium would cause serious pitting corrosion on stainless steel without coating protection, for the passive film of stainless steel could be destroyed by chloride ions. The thin polyphenol coating on the surface of stainless steel prevented the direct contact of chloride ions and steel surface, so the pitting corrosion rate became slow. The corrosion potential of stainless steel in 3.5% NaCl was −0.35 V, and the corrosion current of 4.23 µA was obtained through Tafel fitting. The linear scanning on the polyphenol-coated stainless steel electrodes showed that the corrosion potential became 0.37 V, which had the electrode potential rise of 0.72 V compared with the uncoated anodes. The corrosion current of coated anode was only 0.11 µA which showed a significant reduction, which meant the pitting corrosion resistance of stainless steel was improved. When the electrode potential of phenol polymer coated stainless steel increased to 0.41 V, the anodic current rose sharply. It was inferred that when the anodic electrode potential became high enough, the attraction between the anode and chloride ions became strong, and then the chloride ions got over the polyphenol coating and directly touched the surface of stainless steel, following with the crack of passive film and pitting corrosion. Between the electrode potential of −0.3 and 0.3 V, the polarization current of polyphenol coated stainless steel anode was weaker than the uncoated anode for about two orders of magnitude. The polyphenol coating formed physical isolation between chloride ions and the anode. On the other hand, the existence of large amount of phenol hydroxides made the stainless steel covered by negative charge, so even if the polyphenol coating had cracks or defects, the electrostatic repulsion between phenol ions and chloride ions would also blocked the adsorption of chloride ions on stainless steel surface.

The corrosion potential of polyaniline-coated stainless steel was −0.026 V, and the corrosion current was 0.40 µA. The polyaniline coating also enhance the corrosion resistance of stainless steel against the pitting corrosion. Compared with the naked electrode, the corrosion potential increased to 0.32 V and the corrosion current was one tenth. However, the corrosion resistance of polyaniline was weaker than polyphenol coating. Because polyaniline tended to combine with hydrogen ion and became positive charge carrier even in neutral medium, and this was very different from the electronegative polyphenol coating. Therefore, the electrostatic attraction might promote the adsorption of chloride ions on stainless steel surface, which caused the weaker corrosion protection.

Though the corrosion resistance of polyaniline coating synthesized at the electrode potential of 1.45 V on stainless steel was limited, the electrical polymerization phenomenon of aniline polymerization at the same coating condition of phenol polymerization could be used to form phenol-aniline copolymerization coating and then to change the microstructure of polyphenol coating and reform the coating properties. During the preparation of phenol-aniline copolymerization coating, the amount of aniline was less than phenol for keeping the polymer coating electronegative, so the electrostatic repulsion would still exist between coating and chloride ions, which were helpful for the resistance of pitting corrosion. Depending on the experiment above, a few amount of phenol in the solution was replaced by the same amounts of aniline, and then the corrosion resistance of different phenol-aniline polymer coatings in NaCl medium was tested in order to find out the proper proportion of aniline usage.

C. Phenol-aniline electrochemical copolymerization and the corrosion resistance of copolymer coating

Maintaining the total concentration of phenol and aniline at 0.1 mol/L, the stainless steel anodes were
coated by electropolymer in a series of phenol-aniline solution at the anodic potential of 1.45 V and reaction time of 1 h. Then the corrosion resistance of different polymer coat was compared. The coated anodes were dipped in 3.5% NaCl solution for 0.5 h separately, and the open circuit potentials were recorded. When the solution was 0.1 mol/L phenol without aniline, the open circuit potential was −17 mV. When the solution composition was 95 mmol/L phenol and 5 mmol/L aniline, the open circuit potential of coated stainless steel anodes moved to −47 mV, which showed a poor corrosion resistance, because the close structure of polyphenol coating was disturbed by a few aniline polymer or copolymer. When the phenol concentration was 90 mmol/L and the aniline concentration was 0.01 mol/L, the open circuit potential sharply rose to 21 mV, which was higher than the one observed in 0.1 mol/L phenol solution. This result might be caused by a significant rise of the polymer coating corrosion resistance by the addition of aniline.

In order to seek the proper phenol-aniline proportion, the aniline concentration was increased with the decreasing phenol concentration in the following electropolymerization coating experiments. When the mixture solution was consisted of 87.5 mmol/L phenol and 12.5 mmol/L aniline, the open circuit potential was −44 mV. While the phenol concentration continuously fell to 85, 80, and 50 mmol/L, the open circuit potential of coated stainless steel anodes was falling. When the solution composition was 0.1 mol/L aniline without phenol, the open circuit potential was −79 mV. The polymer coating was thinner because of the difficulty of polymerization in the lower phenol concentration. The negative coating became positive with the increase of aniline proportion, so the electrostatic repulsion of chloride ions disappeared. The absorption of chloride ions led the falling of the open circuit potential. As a result, over usage of aniline and small phenol caused the bad corrosion resistance of the polymer coatings.

The pitting corrosion potentials of a series of phenol-aniline polymer coated stainless steel anode were measured in 3.5% sodium chloride to determine the best corrosion resistance occurred under the solution composition of 0.09 mol/L phenol and 0.01 mol/L aniline, which was chosen by open circuit potential analysis. The coated stainless steel electrodes were dipped in 3.5% sodium chloride solution for 0.5 h, with the nitrogen blasting into the solution, at a scanning rate of 20 mV/min, and the linear scanning was carried out. The larger electrode potentials at the currents of 10 and 100 μA were recorded as pitting corrosion potentials. The relationship between pitting corrosion potentials and different phenol-aniline solution composition was shown as Fig.6. The results showed that the pitting corrosion potential of polymer coating synthesized at 0.09 mol/L phenol and 0.01 mol/L aniline was 0.38 V, which was the maximum pitting corrosion potentials. In addition, this meant the better corrosion resistance. The pitting corrosion potential of 0.1 mol/L phenol coating was 0.22 V, and the pitting corrosion potential of 0.1 mol/L aniline coating was 0.20 V. The curves of open circuit potential and the pitting corrosion potential was similar, and both had the maximum at the solution composition of 0.09 mol/L phenol and 0.01 mol/L aniline. We supposed that at this solution composition, the polymer coating of phenol and aniline not only occurred together, but also formed coating with suitable microstructure for better corrosion resistance.

D. Infrared spectrum analysis of phenol-aniline copolymer

The infrared spectra of phenol polymer and phenol-aniline polymer were similar to each other. In the infrared spectra of polyaniline of former reports [32], the band of N−H stretching vibration was always observed in the region of 3500−3200 cm−1. Since the large amount of hydroxyl in copolymer, the broad band observed at 3388.6 cm−1 in Fig.7 was attributed to the O−H stretching vibration and N−H stretching vibration, which moved towards the low-frequency side compared with the O−H stretching vibration peak of polyphenol. The strong peaks at 1642.0, 1608.7, and 1490.9 cm−1, and the weak peak at 1448.3 cm−1, were related to the aromatic C−C stretching vibrations in phenol-aniline copolymer, which shared the same location and intensity in the infrared spectrums of polyphenol.

The spectrum peak at 1210.8 cm−1 in copolymer was attributed to the C−O stretching vibration of the aromatic ether chain structure, which became weaker than the strong peak in polyphenol at the same wavelength. However, the observation of the medium peak still signified that many benzene rings were coupled by oxygen to form aromatic ethers, which proved that the coating
FIG. 7 Infrared spectrum of phenol polymer and phenol-aniline copolymer.

contained lots of polyphenol structure.

The medium peaks at 1173.6 and 1125.9 cm\(^{-1}\) in copolymer referred to the C–H in-plane deformation vibrations. In polyphenol, because of the covering of C–O stretching vibration peak at 1211.2 cm\(^{-1}\), the C–H in-plane deformation vibrations peak at 1173.6 cm\(^{-1}\) could hardly be observed. The medium peak at 1125.9 cm\(^{-1}\), as the analysis in Refs.[31, 32], referred to the 1, 2, 4-ring substitution, which proved the existence of phenol radical (a) and aniline cation radical (d) shown in Fig.2, and the side chain formation at ortho position of polyaniline and polyphenol. The absorption peak at 1125.9 cm\(^{-1}\) in polyphenol was much weaker than the step-like peak at 1173.6 cm\(^{-1}\), which showed the significant difference between polyphenol and polyaniline. The addition of aniline notably increased the number of side chain, which could cause the compaction of the polymer coating and enhance the corrosion resistance.

The weak peak at 977.7 cm\(^{-1}\) in phenol-aniline copolymer was attributed to the N–O stretching vibration, which showed the coupling in polymerization could also occurred between the radicals (b) and (e) in Fig.2 through the formation of N–O band. Other researcher mentioned the observation of N–O stretching vibrations [33]. The weak peak at 977.7 cm\(^{-1}\) proved the copolymerization of phenol and aniline, and the N–O banding enhanced the corrosion resistance of coating for the coupling of different polymer chains. The medium peaks at 832.8 and 753.7 cm\(^{-1}\) in copolymer were attributed to the out-of-plane deviational vibrations, when the number of adjacent aromatic hydrogens was two and four. These meant that the head-to-ortho and head-to-tail linkages coexisted in the growth of phenol-aniline copolymerization as same as in polyphenol. The medium peak at 694.0 cm\(^{-1}\) in copolymer referred to the N–H wagging vibrations in secondary amine structure, which showed that benzene rings were coupled by nitrogen and formed secondary amine. So the aniline was proved taking part in the phenol-aniline electrochemical copolymerization, and the polyaniline structure was contained in the copolymer coating.

E. SEM analysis of phenol-aniline copolymer coating

In order to study the phenomenon of the pitting corrosion resistance rise of phenol-aniline copolymer coating, the stainless steel anodes, coated in 0.01 mol/L aniline and 0.09 mol/L phenol solution, was cleaned by distilled water, and analyzed by SEM, with the micrographs shown in Fig.8 (a) and (b), compared with the polyphenol coating micrograph at the same enlargement factor in our former report [23]. The copolymer coating was much smoother than the polyphenol coating, and the parallel stria of the coating was not so clear, at the same time the number, the length and the depth of film crack was decreasing. The micrograph could explain the corrosion resistance rise of phenol-aniline copolymer film. As same as the polyphenol film, the cracks were also observed on the copolymer coating, because of the deformation of stainless steel anodes. However, the cracks did not grow along the parallel stria, which showed a better connection in every directions of the coating. Figure 8(b) focused on the cracks of phenol-aniline copolymer coating. The surface of copolymer film waved, composed of copolymer blocks with the diameter of 100 nm. From the side of cracks, the layers and holes were not observed, so the copolymer coating was proved to be more compacted.

Taking advantage of the part solubility of phenol-aniline copolymer in THF, the copolymer film was cleaned by THF, in order to remove the low polymer and monomer, following with the SEM analysis, shown as Fig.8 (c) and (d). The coating shown in Fig.8(c) was much smoother than the uncleaned coating, however, many cracks formed with the solution of THF. Com-
pared with the micrographs of polyphenol film cleaned with THF [23], the most significant difference was the bifurcate network structure that appeared outside or inside the copolymer coating. For the electropolymerization potential of aniline was much lower than phenol, and at the same electrode potential the polymerization of aniline occurred at a much higher reaction rate. Therefore, the bifurcate network structure shown in Fig.8(c), which was the minority of the coating, should be supposed to be mainly composed from polyaniline, with a few phenol chain elements. The molecule structure of phenol-aniline copolymer with bifurcate network structure was shown in Fig.9(a). The bifurcate network structure should be attributed to the 1, 2, 4-ring substitution in the copolymer, which came to the same conclusion of our infrared spectrum analysis.

The micrograph of Fig.8(d) after the copolymer film was cleaned by THF. The micrograph of Fig.8(e) and (f), which was also taken after cleaning by THF, was cited from our former report [23]. The comparison of these two micrographs showed the coating microstructure changed a lot because of the addition of aniline in the electropolymerization processes. Polyphenol coating grew in layers with the weak connection between layers, and the polyphenol layers became curled with the solvent effects, further more, the polyphenol layers was composed of small polymer flakes with the filling of low polymers and monomers. There were no such flake-
like structure observed on the THF cleaned copolymer coating, and the relatively rapid electropolymerization of aniline broke the polyphenol flakes and provided the chemical connection, which synthesized a whole copolymer coating. The layers of the copolymer parallel to the electrode were not notable, so was the curl of coating surface after the solvent effects. It referred that coating growth was not layer-by-layer, so the connection between layers vertical to the anode surface became stronger because of the synthesis of bifurcate network structure.

Through the analysis of SEM results, the microstructure and the growing processes of the phenol-aniline copolymer coating could be supposed as shown in Fig.9(b), and similar structure was mentioned by other researchers [28, 30, 33]. Since the electropolymerization potential of polyaniline was lower than polyphenol, during the coating processes of copolymer, the bifurcate network structure was mainly composed from polyaniline and firstly synthesized on the anode surface, shown as the black irregular curves in Fig.9(b). Then in the later electropolymerization processes, the copolymer of aniline and phenol filled in the interspaces of the bifurcate network structure. At last, the full and smooth phenol-aniline copolymer coating was synthesized on the stainless steel anode surface. Addition of aniline achieved the synthesis of phenol-aniline copolymer coating, and the structure reformation of polyphenol coating was accomplished, which enhanced the pitting corrosion resistance.

Proper quantities of copolymer with bifurcate network structure were supposed to be the skeletal substance in the copolymer coating, which formed a compact coating structure and strong connection. The addition of aniline also enriched the styles of radicals during the processes of electropolymerization, through the coupling of different radicals the flake-like structure of polyphenol was changed and connected together, which was helpful to synthesize a copolymer coating with better smoothness, less cracks and higher corrosion resistance. More or less quantities of aniline would both cause the falling of corrosion resistance. With less aniline quantities the bifurcate network structure could not be generated enough in coating, the skeletal effects would be weaker, but the flake-layer structure of polyphenol has been destroyed by aniline addition, so the pitting corrosion resistance became worse. If more aniline was added into the reaction system, the network structure would develop too much, so there would be not enough polyphenol filling the interspaces among the network structure. The loose structure of copolymer would also make the corrosion resistance decrease. Only keeping the proportion of phenol and aniline at 9/1, and the perfect copolymer coating was synthesized on stainless steel anodes. The proportion of phenol and aniline created the best cooperation of copolymer with network structure and filling structure, which mostly raised the pitting corrosion potential.

**IV. CONCLUSION**

The polyphenol coating on 304 stainless steel anodes was synthesized in 0.1 mol/L phenol solution, using 0.1 mol/L Na₂SO₄ as electrolyte, with the anodic electrode potential of 1.45 V, the bath voltage between anode and cathode of 2.5V and the reaction time of 1 h. The phenol coating notably enhanced the pitting corrosion resistance of 304 stainless steel in 3.5% NaCl, since the pitting corrosion potential of polyphenol-coated anodes was 0.224 V. Keeping the sum of phenol and aniline concentration at 0.1 mol/L, the phenol-aniline copolymer coating was synthesized at the same electrochemical condition on 304 stainless steel anodes. When the solution contained 0.09 mol/L phenol and 0.01 mol/L aniline, the copolymer coating achieved the best pitting corrosion resistance, while the pitting corrosion potential in 3.5% NaCl increased to 382 mV as well as the rise of open circuit potential.

Through the infrared spectrum comparison of phenol polymer and phenol-aniline copolymer coatings, the polyaniline structure was proved in the copolymer, and the reasons of the corrosion resistance enhancement were discussed. There were more 1,2,4-ring substitution reactions occurring in phenol-aniline copolymer than polyphenol, which caused more side chains generated during the electropolymerization and a much more compact coating product. The connection between phenol and aniline monomers during the growth of copolymer included several ways, including aromatic ethers, secondary amine and nitrogen-oxygen bonding.

Taking advantage of the part solubility of polyphenol and polyaniline in THF, SEM was used to analyze the microstructure of phenol-aniline copolymer coating, with the comparison of polyphenol coating. Polyphenol coating grew layer-by-layer, and each layer was composed of polyphenol flakes with the diameter of 50 nm. The weak connection between layers and flakes would cause cracks growing easily in polyphenol coating. In the copolymer coating cleaned by THF synthesized at proper phenol-aniline proportion, the bifurcate network structure was observed, which was mainly composed from polyvinyl, with other copolymer, mainly polyphenol, filling the interspaces. The network structure in copolymer coating worked as skeletal substance, restraining the growth of cracks, enhancing the connection between layers. The flake-like structure did not appear in copolymer coating. As a result, the pitting corrosion resistance against chloride ions was further raised through the addition of aniline and the copolymerization of phenol and aniline.