

Effects of Sulfanilic Acid and Anthranilic Acid on Electrochemical Stability of Polyaniline

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Polyaniline (PANI) as active material of batteries possesses excellent electrochemical reversibility. It is a promising candidate for a rechargeable battery with a high performance. However, the electrochemical degradation of polyaniline becomes a bottleneck of PANI battery. The sulfanilic acid and anthranilic acid as two kinds of additives were used to inhibit the degradation of polyaniline. The polyaniline was deposited onto the platinum electrode by the cyclic voltammetry in 1.0 M sulfuric acid solution containing 0.2 M aniline and different concentrations of sulfanilic acid or anthranilic acid. The electrochemical degradation of polyaniline was studied in 1.0 M sulfuric acid solution at 25 °C. The electrochemical experimental results show that when the concentrations of sulfanilic acid and anthranilic acid are respectively 0.02 M and 0.04 M, the inhibition of the degradation of polyaniline can reach 13.8 % and 11.2 % in 1.0 M sulfuric acid solution, respectively. The morphology, structure and electrochemical properties of polyaniline before and after adding sulfanilic acid and anthranilic acid were also studied.

Keywords: Polyaniline, Sulfanilic acid, Anthranilic acid, Degradation, Inhibition

1. INTRODUCTION

Polyaniline as a kind of conductive polymer has important applications. Polyaniline has been one of research hot spots that attract many scholars in recent decades because of its good electrochemical behavior, excellent redox and electrochromic properties, unique doping and dedoping properties, good environmental stability and simple synthesis methods. Now polyaniline are widely

used as electrode materials of the secondary battery [1, 2], chemical and biological sensors [3, 4], electrochromic display devices [5] and metal corrosion protection [6], etc. Degradation of polyaniline has always been one of the major barriers when it is used as the base materials [7, 8]. Therefore, many researchers paid more attentions to study the stability and degradation of polyaniline [9-11].

The researches on the polyaniline degradation mainly include two aspects, the mechanism and the inhibition of polyaniline degradation. Malinauskas *et al* studied the kinetics of electrochemical degradation of polyaniline and found that the degradation proceeds faster in more acidic solutions and follows the first-order reaction kinetics [12, 13]. They also found that the degradation rate of polyaniline depends greatly on the electrode potential applied [14]. Stilwell *et al* carried out electrochemical studies on degradation reaction of oxidized polyaniline and identified *p*-benzoquinone as a major soluble degradation product [15]. Arsov *et al* gave a discussion of degradation mechanism and found the degradation products of polyaniline including benzoquinone, aminophenol, hydroquinone and quinoneimine [16].

Many methods were used to inhibit the degradation of polyaniline, such as incorporating doping ions into conducting polymers, adding specific additives in the solution, and modifying the structure of polyaniline. Zagal *et al* suggested that the presence of FeEDTA (ethylenediamine tetraacetic acid ferric salts) can inhibit the second redox process in the polyaniline film corresponding to the emeraldine/permanganine transition and decrease degradation of the polyaniline film at positive potentials [17]. Rahmanifar *et al* reported that the polymerization of aniline in the presence of anionic surfactants such as SDS (sodium dodecylsulfate) and SDBS (sodium dodecylbenzenesulfonate) can lead to the polyaniline films having improved characteristics and the PANI-DS⁻ (dodecylsulfate) film reveals a good resistance against the electrochemical degradation [18]. Gao *et al* found that those quinone-like molecules such as hydroquinone produced during degradation can endow polyaniline with some resistance to over-oxidation and protect it from further degradation [19]. Cui *et al* reported that the extent of degradation of aniline-metanilic acid copolymer was less than that of polyaniline, which was interpreted that the presence of sulphonate curtailed the bipolaron production and increased the steric hindrance in degradative hydrolysis [20].

In this paper, we continued to seek to the additives that could inhibit the degradation of polyaniline, mainly studied the effects of sulfanilic acid and anthranilic acid on the degradation of polyaniline. The sulfanilic acid and anthranilic acid as two kinds of functionalized protonic acid are denoted as H⁺(M⁻-R), where H⁺M⁻ is protonic acid group such as sulfonic acid and carboxylic acid; and R is an organic group. The protons of sulfanilic acid and anthranilic acid react with imine nitrogens of polyaniline and convert the base form to the conducting salt form of polyaniline; the sulfanilic and anthranilic groups serve as the counter-ions in the polyaniline. The larger molecules of the counter-ions can shield the bipolarons from nucleophilic attack by OH⁻ ions or H₂O molecules in aqueous solutions to improve the stability of the polyaniline. And the electrochemical experimental results show that when the concentration of sulfanilic acid and anthranilic acid are respectively 0.02 M and 0.04 M, the inhibition of polyaniline degradation reach 13.8 % and 11.2 % in 1.0 M sulfuric acid

solution at 25 °C, respectively. The polyaniline containing 0.02 M sulfanilic acid, 0.04 M anthranilic acid and no additives were marked S-PANI-4, A-PANI-4 and PANI, respectively. We also studied the morphology, structure and electrochemical properties of S-PANI-4, A-PANI-4 and PANI.

2. EXPERIMENTAL

2.1. Chemicals

Aniline, sulfuric acid (H₂SO₄), sulfanilic acid and N,N-dimethylformamid (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Anthranilic acid was supplied by Taicang Guangyao Reagent Factory (Jiangsu, China). All chemicals used were analytical grade. The monomer aniline was distilled under reduced pressure and stored in refrigerator (about 4 °C) before use. All aqueous solutions were prepared using doubly distilled water.

2.2. Electropolymerization of polyaniline films

The electropolymerization of the aniline was performed on CHI 660D electrochemical workstation (CHI Instruments, USA) in a three-electrode system, containing 5mm×5mm platinum plate as a working electrode, 10mm×10mm platinum plate as a counter electrode, and saturated calomel electrode (SCE) as a reference electrode. All potentials reported are referred to this reference electrode. PANI films were prepared on the platinum working electrode by the cyclic voltammetry within the potential of -0.2 V to 1.0 V for 10 cycles in a solution containing 0.2 M aniline, 1.0 M sulfuric acid and different concentrations of sulfanilic acid (0.005M, 0.01M, 0.015M, 0.02M, 0.025M, 0.03M) or anthranilic acid (0.01M, 0.02M, 0.03M, 0.04M, 0.05M, 0.06M). And the potential scan rate of electropolymerization is controlled at 50 mV/s. After the electropolymerization of the aniline, the polyaniline electrode was repeatedly washed with acetone and the doubly distilled water until the washing liquid was completely colorless, and dried at 50 °C finally. The degradation products during the polymerization of aniline can be removed.

2.3. Electrochemical degradation of polyaniline films

The electrochemical degradation was performed on a CHI 660D electrochemical workstation by the cyclic voltammetry within the potential limits of -0.2 V to 1.0 V for 30 cycles in the 1.0 M sulfuric solution at 25 °C. The potential scan rate of the electrochemical degradation is controlled at 20 mV/s. The polyaniline degradation time was just 10 minutes for 5 cycles. In our study, a high limit of 1.0 V is chosen to shorten the reaction time and observe the effects of additives on the degradation of the polyaniline more clearly. So the experiment was operated in 1.0 M H₂SO₄ solution in the range of -

0.2 V~1.0 V. The peak current of the first anodic peak of polyaniline was taken into account and used in the following calculations. The sulfuric acid solution after the degradation process was collected and measured by UV-vis spectrophotometer (Shimadzu UV-2550) in the range of 200~600 nm at room temperature.

2.4. Characterization of polyaniline samples

The impedance spectroscopy (EIS) was recorded at the opening circuit potential (OCP) in the frequency range from 10000 to 0.1 Hz with an amplitude of 10 mV in the electrochemical workstation (AutoLab, Nova 1.9, Metrohm). The charge and discharge of polyaniline half-cell were also performed in the range of 0 ~ 0.7 V with the 2 mA/cm² of current density by Chronopotentiometry on a CHI 660D electrochemical workstation in a three-electrode system. The polyaniline samples were dissolved in the DMF and measured in the range of 200 ~ 800 nm by UV-vis spectrophotometer (Shimadzu UV-2550) at room temperature. The diffraction patterns of the samples were measured by X-ray diffraction (XRD, D8 Advance, Bruker-AXS) at room temperature, covering angles 2 θ between 10° and 80°. A Hitachi S-4800 scanning electron microscopy (SEM) was used to examine the surface morphologies of the polyaniline.

3. RESULTS AND DISCUSSION

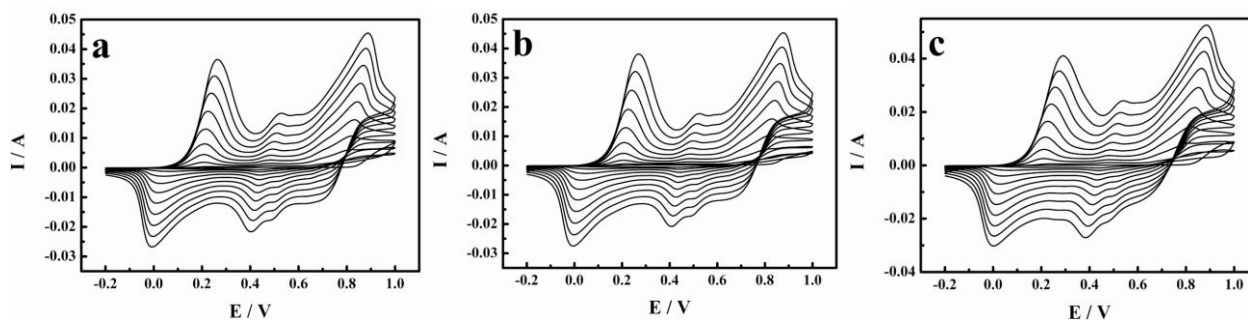


Figure 1. Electropolymerization of aniline on a Pt electrode surface in aqueous 1.0 M H₂SO₄ + 0.2 M C₆H₅NH₂ solution containing no additives (a), a certain amount of sulfanilic acid (b) and anthranilic acid (c).

Figure 1a shows the cyclic voltammograms of the polyaniline film growth from the solution consisting of 0.2 M aniline and 1.0 M H₂SO₄. The peak current increased with the increase of the number of cycles. Electropolymerization of aniline goes through an induction period, in which aniline is oxidized to aniline radical cation firstly, and then the radical cations are polymerized to form oligomer of aniline and finally the polyaniline is generated by autocatalytic reaction [21, 22]. The protonation is the most important condition to generate conductive polyaniline during electrochemical

polymerization of aniline. The peak current of polyaniline slightly increased and the peak shape of polyaniline unchanged after adding a certain amount of sulfanilic acid and anthranilic acid (Figure 1b, c).

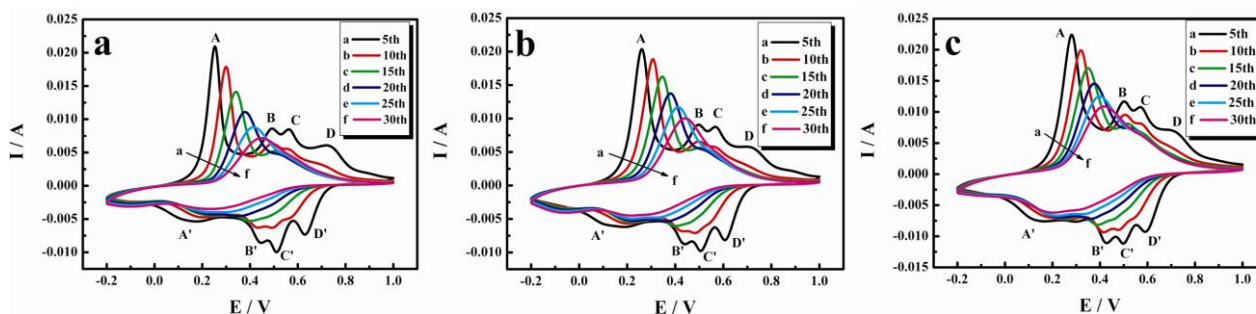


Figure 2. Cyclic voltammograms of polyaniline degradation in the different cycles in the 1.0 M sulfuric acid solution. (a) PANI; (b) S-PANI; (c) A-PANI.

In the cyclic voltammograms of the polyaniline (Figure 2a), there are four pairs of redox peaks [16], which are respectively the redox peaks of fully reduced (leucoemeraldine) form and the intermediate oxidation (emeraldine) form of polyaniline (A and A' peaks) at 0.2 V, the redox peaks of benzoquinone and hydroquinone (B and B' peaks) at 0.4-0.5 V, the redox peak of *p*-aminophenol and benzoquinoneimine (C and C' peaks) at 0.5-0.6 V, and the redox peak of intermediate oxidation form and the fully oxidized (pernigraniline) form (D and D' peaks) at 0.6-0.7 V [23, 24]. The two peaks in the middle were caused by the degradation products. With the degradation of polyaniline proceeding, the electrochemical activity of polyaniline gradually weakened and the characterized redox peaks (A and A' peaks; D and D' peaks) weakened or disappeared. In addition, as the number of cycles increased, the A peak moved towards the lower potential gradually, which was caused by different oxidation states or different structures of polyaniline after the degradation. The relative peak current ($I_{p,A}$) is used to evaluate the extent of electrochemical degradation of the polyaniline [25].

Though three kinds of polyaniline (PANI, S-PANI and A-PANI) had a similar degradation behavior, the change of the peak current of S-PANI and A-PANI was significantly smaller than that of PANI. We presented the fifth scan of cyclic voltammograms of PANI to avoid low reproducibility of the first scan (Figure 2b, c). The peak current of the first anodic peak in the 5th, 10th, 15th, 20th, 25th and 30th cycles were chosen to study the kinetics of polyaniline degradation. Taking into account the effects of additives on the amount of deposited polyaniline, the relative peak current ($I_{p,A}$) is used to evaluate the extent of electrochemical degradation of the polyaniline. Considering the reproducibility of the cycle curves, the peak current in the 5th, $I_{p,A}(5)$, is used as the reference standard. So the relative peak current of the *n* cycle is taken as the ratio of $I_{p,A}(n)$ to $I_{p,A}(5)$. The results of the relative peak current values that calculated in this way are more accurate and reliable.

Table 1. Change of the relative peak current of the first anodic peak of polyaniline doped with different concentrations of sulfanilic acid

Entry	Blank	0.005 M	0.010 M	0.015 M	0.020 M	0.025 M	0.030 M
5	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10	0.839	0.870	0.876	0.907	0.908	0.916	0.883
15	0.656	0.704	0.721	0.765	0.770	0.766	0.743
20	0.509	0.562	0.585	0.633	0.639	0.635	0.623
25	0.397	0.447	0.475	0.518	0.532	0.529	0.527
30	0.304	0.353	0.386	0.423	0.442	0.441	0.446

Table 2. Change of the relative peak current of the first anodic peak of polyaniline doped with different concentrations of anthranilic acid

Entry	Blank	0.01 M	0.02M	0.03M	0.04 M	0.05 M	0.06M
5	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10	0.839	0.834	0.854	0.865	0.863	0.861	0.856
15	0.656	0.680	0.717	0.728	0.720	0.712	0.707
20	0.509	0.560	0.593	0.606	0.598	0.588	0.585
25	0.397	0.453	0.488	0.502	0.499	0.489	0.482
30	0.304	0.362	0.400	0.412	0.416	0.407	0.403

The change of the relative peak current of the first anodic peak of polyaniline doped with different concentrations of sulfanilic acid was shown in Table 1. With the increase of redox cycles, the relative peak current of the first anodic peak of polyaniline decreased. If sulfanilic acid was not added, the relative peak current of the anodic peak of polyaniline in the 30th cycle reduced to 30.4% of that in the 5th cycle. However, with the increase of the concentrations of sulfanilic acid, it was found that the relative peak current of the anodic peak of polyaniline in the 30th cycle gradually increased, which indicated that the addition of a certain amount of sulfanilic acid during the polymerization process of aniline can inhibit the degradation of polyaniline. While the concentrations of sulfanilic acid were higher than 0.02 M, the relative peak current of the anodic peak of polyaniline in the 30th cycle no longer increased. So when the concentration of added sulfanilic acid is 0.02 M, the inhibition of the polyaniline degradation can reach 13.8 %.

The change of the relative peak current of the first anodic peak of polyaniline with different concentrations of anthranilic acid was shown in Table 2. With the increase of the concentrations of anthranilic acid, the relative peak current of the anodic peak of polyaniline in the 30th cycle gradually increased, so the addition of a certain amount of anthranilic acid during the polymerization of aniline can inhibit the degradation of polyaniline, too. While the concentrations of anthranilic acid were higher than 0.04 M, the relative peak current of the anodic peak of polyaniline in the 30th cycle no longer increased, and decreased instead. Therefore, when the concentration of added anthranilic acid is 0.04 M, the inhibition of the polyaniline degradation can reach 11.2 %.

The sulfanilic and anthranilic group as counter-ions can be doped into polyaniline in the polymerization of aniline [26, 27]. The protons doped into polyaniline chains during the charge process, and the proton dedoped from the polyaniline chains during the discharge process. The doping and dedoping processes are a dynamic equilibrium during the charge and discharge processes. Therefore, there was a mutual conversion between polyaniline salts and polyaniline bases. The polyaniline base is more stable than polyaniline salt, since the polyaniline degradation is due to the nucleophilic attack to polyaniline salts by OH^- ions or H_2O molecules [28]. The larger molecules of the counter-ions such as sulfanilic and anthranilic ions can shield the bipolarons better than the sulphate ions from nucleophilic attack of OH^- ions or H_2O molecules in aqueous solutions [29, 30]. In addition, a polyaniline unit is only doped with a sulphate ion, while a polyaniline unit is doped with two sulfanilic ions or anthranilic ions [30]. So the polyaniline doped with sulphate ions is instability and the sulphate ion is prone to dedope from the polyaniline chain, which results in the weakening of the electrochemical activity of polyaniline. Since the polyaniline presents “compact coil” structure, the larger anions (sulfanilic and anthranilic anions) may not enter into the solution during the dedoping process, and sulfanilic and anthranilic anions can be retained in the “compact coil” structure of polyaniline instead. The sulfanilic and anthranilic anions may be doped into the polyaniline chains again during reduction process [31].

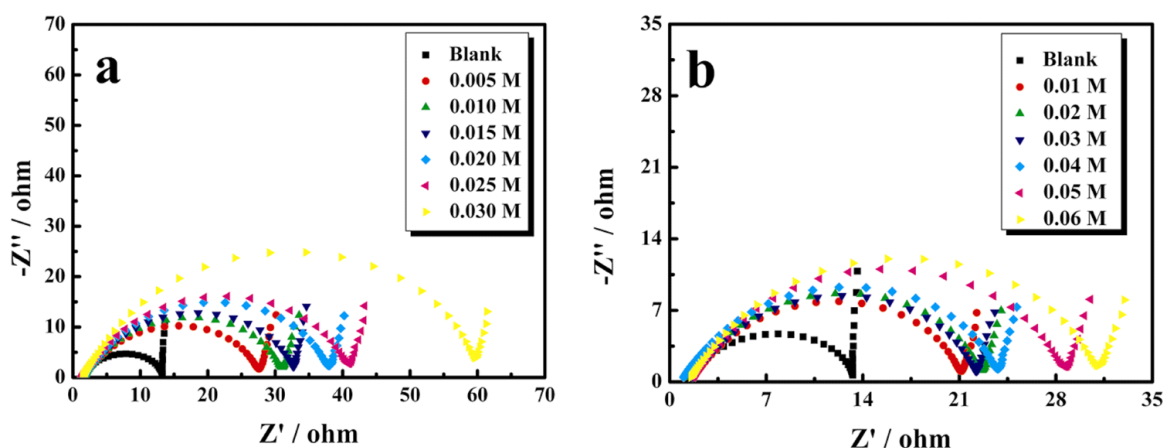


Figure 3. Impedance spectroscopy for the polyaniline after adding different amounts of sulfanilic acid (a) and anthranilic acid (b) in the 1.0 M sulfuric acid solution.

Nyquist diagrams for the polyaniline after adding different concentrations of sulfanilic acid and anthranilic acid were shown in Figure 3a and Figure 3b, respectively. All curves contained a semicircle and a line, and the diameter of these semicircles increased with increasing concentrations of the additives. The semicircles at the high frequency region were attributed to the double layer capacitance in parallel with the charge transfer resistance (R_{ct}) due to the ion exchange for charge compensation at the polyaniline-electrolyte interface, and the R_{ct} increased with the increasing concentrations of sulfanilic acid and anthranilic acid [32, 33]. In the meanwhile, the vertical line indicated that the property of the system was close to an ideal capacitance (the faradaic pseudocapacitance of the

polyaniline) behavior in the absence of additives and the electrode process was mainly controlled by charge transfer process (electrochemical reaction steps) [34]. When there were additives, it not only led to increased R_{ct} with increasing amounts of additives, but also the angles of the lines presented 45° at the low frequency, which was caused by irregular geometry of the polyaniline electrode surface. And the electrode process was controlled by charge transfer and Warburg diffusion processes at this point [34, 35].

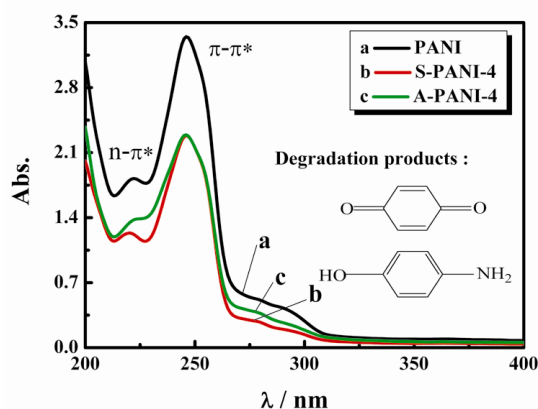


Figure 4. UV-vis spectra of sulfuric acid solutions after the degradation.

The soluble degradation products of polyaniline in the sulfuric acid solutions include *p*-benzoquinone, *p*-aminophenol, and dimmers and oligomers from the shortening of polymer chains, and *p*-benzoquinone is unstable in the sulfuric acid solutions and translated into aniline. All the UV-vis spectra of sulfuric acid solutions after the degradation process had two absorption peaks (Figure 4), which respectively related to π - π^* transition at 246 nm [15] and n - π^* transition at 220 nm in the benzenoid structure of *p*-aminophenol and aniline. The absorbance of curve (b) and curve (c) was smaller than that of curve (a), which further indicated that sulfanilic acid and anthranilic acid can inhibit the degradation of polyaniline. The results are consistent with the results revealed in Table 1 and Table 2.

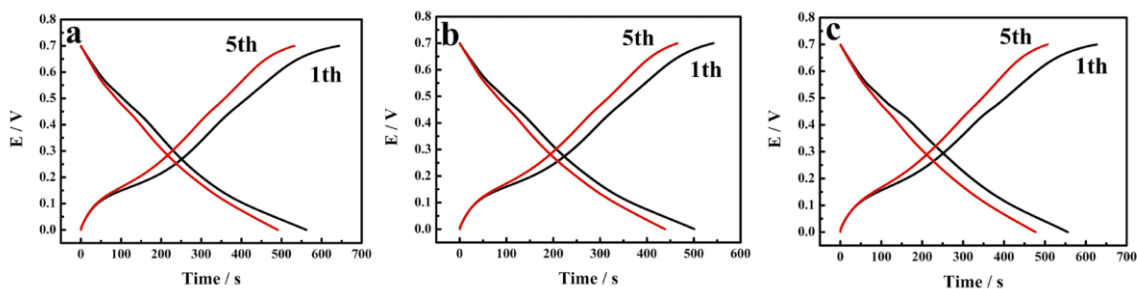


Figure 5. The charge and discharge curves (the first cycle and the fifth cycle) of polyaniline half-cell in the 1.0 M sulfuric acid solution at 25 °C (a: PANI; b: S-PANI-4; c: A-PANI-4).

Figure 5a-c showed the charge and discharge curves of three kinds of polyaniline half-cell at 25 °C. All charge-discharge curves of polyaniline had good symmetry, which suggested the polyaniline after adding sulfanilic acid or anthranilic acid still had good charge and discharge reversibility. Only the emeraldine form after the proton doping shows the electrical conductivity. While the leucoemeraldine form and pernigraniline form cannot be doped with proton, and they don't show the electrical conductivity, either. The emeraldine form (i.e. oxidized leucoemeraldine form) is doped with the proton to form polyaniline salts at higher potentials, and the dedoped emeraldine transfers to the leucoemeraldine form via the reduction reaction at low potentials. The charge and discharge processes are reversible under a certain condition. All those suggest that sulfanilic acid and anthranilic acid as additives do not affect doping-dedoping or charge-discharge performances. The conductivity of S-PANI-4, A-PANI-4 and PANI was measured by the four-probe technique, the results showed that conductivity of S-PANI-4, A-PANI-4 and PANI were $1.557 \text{ S}\cdot\text{cm}^{-1}$, $0.786 \text{ S}\cdot\text{cm}^{-1}$ and $1.571 \text{ S}\cdot\text{cm}^{-1}$, respectively.

The UV-vis spectra of PANI, S-PANI-4 and A-PANI-4 were presented in Figure 6. The UV-vis spectrum of PANI showed two strong absorption peaks at 331 nm and 619 nm, which were respectively attributed to π - π^* transition in the benzenoid ring and exciton absorption due to polaron/bipolaron transition in the doped polyaniline [36].

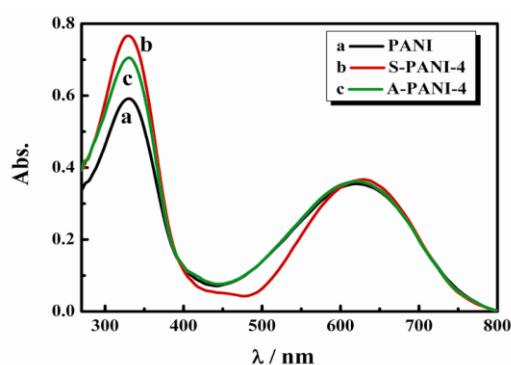


Figure 6. UV-vis spectra of three kinds of polyaniline (PANI, S-PANI-4 and A-PANI-4).

Peak observed at 619 nm for PANI showed a red shift in S-PANI-4 (632 nm) and A-PANI-4 (622 nm) indicating partial reduction of the polymer backbone [37], which suggested that both of polyaniline doped with sulfanilic acid and anthranilic acid had steric effect on the polyaniline chains and the oxidant molecules could not approach the polyaniline chains. So the oxidation extent of the polymer chains of S-PANI-4 and A-PANI-4 were lower than that of the PANI under the same conditions. The sulfanilic acid as dopants resulted in a greater steric effect on the polyaniline chains.

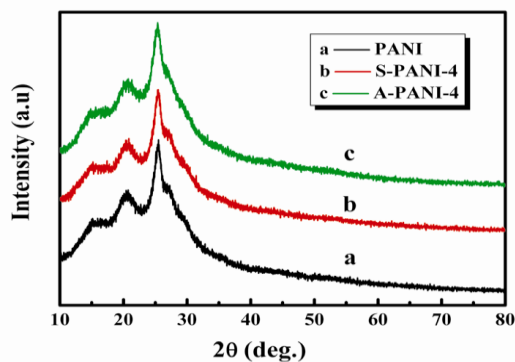


Figure 7. XRD patterns of PANI, S-PANI-4 and A-PANI-4.

The X-ray diffraction patterns of PANI, S-PANI-4 and A-PANI-4 were shown in Figure 7. They all had three diffraction peaks in 2θ from 10° to 80° [38-40], which suggested that the structure of PANI, S-PANI-4 and A-PANI-4 existed partial crystallization. The diffraction peak at ca. $2\theta \sim 15^\circ$ was corresponding to the scattering parallel to the polymer chains. The diffraction peak at ca. $2\theta \sim 20^\circ$ was the characteristic diffraction of the amorphous polymer, which was related to scattering between adjacent surfaces of the benzene or adjacent chains of polymer. And the diffraction peak at ca. $2\theta \sim 25^\circ$ was attributable to periodicity scattering perpendicular to the polymer chains. A small amount of sulfanilic acid and anthranilic acid had little effect on the crystal form and structure of the polyaniline and the results did not show up in the XRD patterns. In other words, the adding of sulfanilic acid and anthranilic acid had little effect the conductive structure of polyaniline.

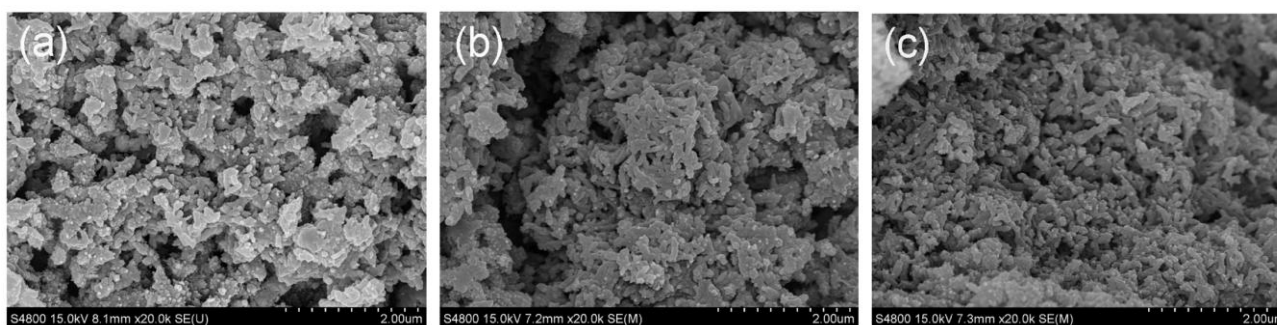


Figure 8. SEM images of PANI (a), S-PANI-4 (b) and A-PANI-4 (c).

The morphologies of the PANI, S-PANI-4 and A-PANI-4 were analyzed by SEM and their photographs were shown in Figure 8. It can be seen that the polyaniline shows lamellar structure and this kind of loose structure has many pores, which is advantageous to the electron transfer processes and doping and dedoping processes of the anions. After adding the additives of sulfanilic acid and anthranilic acid, the morphology of the polymer presented striped structure and remained porous

structure. It was found that three kinds of the polyaniline were piled up by the small particles. So adding the additives of sulfanilic acid and anthranilic acid influenced the way of aggregation of the particles in the polymer and did not change the nature of polyaniline. Additionally, the polymerization of aniline occurs in an ordered manner after adding the sulfanilic acid and anthranilic acid, making the aggregation of the particles more closely, relative to PANI.

4. CONCLUSIONS

Sulfanilic acid and anthranilic acid as additives were used to inhibit the degradation of polyaniline. The electrochemical experimental results show that when the concentration of sulfanilic acid and anthranilic acid are 0.02 M and 0.04 M, the inhibition of degradation extent of polyaniline can reach 13.8 % and 11.2 % in 1.0 M sulfuric acid solution, respectively. The larger molecules of sulfanilic and anthranilic ions as the counter-ions can shield the bipolarons better than the sulphate ions from nucleophilic attack of OH⁻ ions or H₂O molecules in aqueous solutions. According to a variety of morphology, structure and electrochemical characterizations of S-PANI-4 and A-PANI-4 and PANI, it is found that sulfanilic acid and anthranilic acid as additives do not affect the charge-discharge performances and the nature of the polyaniline. The S-PANI-4 and A-PANI-4 have better electrochemical stability than PANI.

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