

Influence of Dopant on Electroactivity of Polyaniline

Yanyan Wang, Kalle Levon*

Summary: Polyaniline (PANI) films were polymerized on glass carbon (GC) electrodes with small molecular dopants hydrochloric, perchloric, sulfuric, methanesulfonic, benzenesulfonic, *p*-toluenesulfonic and large macromolecular size poly(4-styrenesulfonic (PSS)), poly(vinylsulfonic), poly(acrylic), and poly(anilinesulfonic) acids. Their redox electroactivities were studied in buffered solutions with the pH of 3, 5, 7, and 9. Results indicated that the properties of PANI films were strongly dependent on the molecular size and polar characteristics of the dopants. With the polyelectrolytes, it was found that the PANI doped with PSS showed a good redox behavior, and maintained the inherent electroactivity of PANI in the neutral and even in alkaline media.

Keywords: dopant; electroactivity; polyaniline

Introduction

Polyaniline (PANI) has been investigated intensively over the past decades due to its unique electrical properties and its reversible control of either redox or protonic doping.^[1–4] The electroactivity of PANI can be induced by protonation of the imine sites on the main PANI chain using acidic dopants as the insulating emeraldine base form of PANI becomes a conductive emeraldine salt.^[5–7] The increase in conductivity induced by doping can be of ten orders of magnitude or more. Numerous studies had been performed to dope PANI with various dopants to enhance the stability and conductivity of PANI (^[8–10]). The protonated PANI complexes will contain small counter anions which can be exchanged with the other small anions or macromolecular anions, or macromolecular counterions which are non-exchangeable with the PANI matrix. Many results also indicate that the mechanism of electro polymerization of aniline impacts the function of the dopants.^[11,12] Therefore, studies on the electropolymerization of aniline with various dopants are potentially important.

In spite of the importance of the electrochemical synthesis of PANI in the presence of various dopants, there are remaining controversies about the effect of the pH on the behavior of the polymer.^[13] The emeraldine salt form of PANI has been characterized with a change in conductivity in response to a pH change. As the pH is increased, dedoping of the polymer occurs causing a transition from the emeraldine salt to emeraldine base form with the simultaneous conductivity decrease.^[14] The pH sensitivity of PANI is an important issue from the sensor design point of view.^[6,15–17] The PANI film responses to pH changes are quite complicated, being at least partly dependent on the kind of dopant.^[18] Therefore, it is meaningful to investigate the relation between the pH sensitivity and the nature of the dopants.

In this article, our aim is to gain a deeper insight into the electroactivity of the PANI. The polymerization of PANI on glass carbon (GC) electrode (the rate of PANI film growth on hydrophobic surfaces is higher than it is on hydrophilic^[19]) with different dopants by cyclic voltammetry (CV) methods are reported. The electrochemical synthesis of conductive polymers allows preparation of layers of polymers of

Polytechnic Institute of NYU, Brooklyn, NY 11201, USA
E-mail: klevon@poly.edu

desired thickness, shape and dimensions that, generally, are not possible by chemical methods.^[20] To test the pH range over which the PANI protonic doping mechanism is active, the doping and supporting electrolyte anions' effect on changes of solution pH were systematically studied.

Experimental Part

Reagent

Aniline, polyaniline (emeraldine base, Mw ~10,000), 1-methyl-2-pyrrolidinone, hydrochloric acid (HA), perchloric acid (PA), sulfuric acid (SA), methanesulfonic acid (MSA), benzene sulfonic acid (BSA), *p*-toluenesulfonic acid (TSA), poly(4-styrenesulfonic acid) (PSSA, Mw 75,000), poly(vinylsulfonic acid) (PVSA), poly(acrylic acid) (PAA, Mw 130,000), and poly(anilinesulfonic acid) (PASA, Mw 10,000) were purchased from Sigma-Aldrich Co. Prior to use, aniline monomer was purified by distillation and stored under nitrogen gas at 4 °C. Unless otherwise mentioned, all other reagents were used as received and the aqueous solutions were prepared by using Milli-Q (Millipore) water.

Aniline Polymerization

For the electrochemical experiments, Platinum was used as counter electrode and reference electrode was Ag/AgCl (1 M KCl), cleaned Glass carbon (3 mm diameter) was used as working electrode. All the electrochemical experiments were carried out on an electrochemical analyzer (CHI 660D, CH Instrument). PANI was electrochemically polymerized on the GC electrode from an aqueous solution containing 0.05 M aniline, 1 M acid or in 0.05 M aniline, 1 M acid as electrolyte and 10 mg/mL polyelectrolyte by CV method; deposition was started by sweeping the potential from –0.2 V to 0.9 V for the first cycle to initiate polymer growth,^[21] and then continuing cycling between –0.2 V to 0.78 V for 59 cycles with a scan rate of 100 mV/S. After the deposition, the resulting films were characterized using CV. Throughout the studies, anaero-

bic conditions were maintained with nitrogen gas atmosphere.

Layer by Layer Assembly Protocol

The concentrations of the PANI and polyelectrolyte solutions were 1 (NMP) and 10 mg/mL, respectively. To assemble PANI/Polyelectrolytes multilayer films, the cleaned GC electrode was dipped in PANI solution for 15 min, followed by rinsing with DI water for 15 s, and soaking in DI water for 5 min. Then the modified electrode was dipped in polyelectrolyte solution for 15 min. This procedure was repeated three times and gently dried under a N₂ stream and immediately mounted in an electrochemical cell.

Evaluation of the pH Sensitivity

The electrochemical redox activities of PANI-coated GC electrodes were evaluated by the CV methods within the pH range of 3–9. A 5 mL solution was used for each reaction. All measurements were made at ambient temperature (about 25 °C). The buffer solution consisted of 0.2 M Na₂HPO₄ and 0.1 M citric acid. pH was adjusted by spiking solutions with 1 M HCl acid or NaOH.

Results and Discussion

Electrochemical Polymerization of PANI

The CV curves recorded during the synthesis of PANI films with dopant H₂SO₄ in two different potential ranges are shown in Figure 1. The PANI-modified GC electrode exhibited two pairs of well-defined redox waves at 0.22 and 0.8 V in 1 M H₂SO₄ solution, which were due to the redox processes of leucoemeraldine/emeraldine and emeraldine/permanganiline, respectively. The wave at around 0.5 V was attributed to the process of degradation products produced by the cover oxidation of the film, by phenazine type groups^[22,23] or by quinoneimine groups.^[24,25] For the polymerization of PANI within potential range between –0.15 V and 0.85 V (Figure 1a), a higher rate of growth can

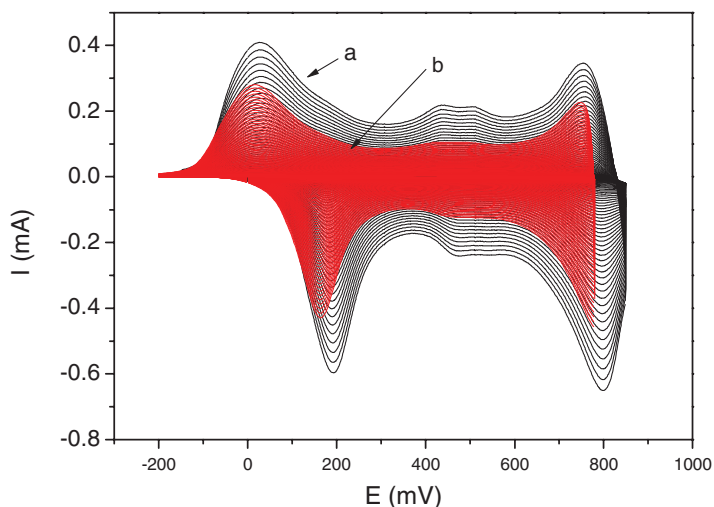


Figure 1.

Cyclic voltammograms of PANI growth on GC electrodes within different potential range. (a) The potential was scanned at -0.15 and 0.85 V; (b) The potential was scanned from -0.20 to 0.9 V for the first cycle, there after, the anodic potential was lowered to $+0.78$ V. Scan rate, 50 mV/s.

be achieved, but at the risk of polymer degradation and other undesired side reactions, which increase the film capacitance and may lead to less-conducting PANI films.^[26] While it is interesting to mention that during the potential cycling almost no intermediate peak related to degradation of the polymer was observed when polymerization of PANI from -0.2 to 0.9 V for the first cycle to nucleation on the electrode surface, and when the cycling continues within -0.2 V and 0.78 V (Figure 1b). The results approved that control of the anodic potential limit is of critical importance to minimize the degradation process, and the lower potentials (0.78 V) can be applied to generate PANI with probably improved quality. In the following experiments, -0.15 V and 0.78 V was used for the polymerization of PANI.

Effect of Dopants on the pH Sensitivity of PANI

PANI, by itself, reveals redox functions only in acid media, $\text{pH} < 3$,^[27] a feature that limits its broad use. It was, however,

reported that the doping of PANI with special anionic species could switch the redox activity of PANI to neutral pH values in aqueous media. Here, we chose small counter ions (HA, PA, SA, MSA, BSA and TSA) which can be easily exchanged, and negatively charged polyelectrolytes (PSSA, PAA, PVSA and PASA), hardly exchangeable to evaluate their effect on the pH sensitivity of PANI.

Effect of Small Counter Ion Dopant

We compared the CVs behavior of PANI doped with HA, PA, SA, MSA, BSA and TSA in pH 3, 5, 7 and 9 (Figure 2). Two anodic oxidation peaks appear at pH 3 and only one reduction peak appears at pH 5 (the peak disappeared for using HA as dopant indicating that the smallest HA ion can be easily released from the polymer). The transfer of the PANI-modified Pt electrode into solutions of pH 7 and 9 results in the disappearance of the oxidation peaks previously observed in these acidic solutions. And as the pH of the solution increased, a continuous decrease

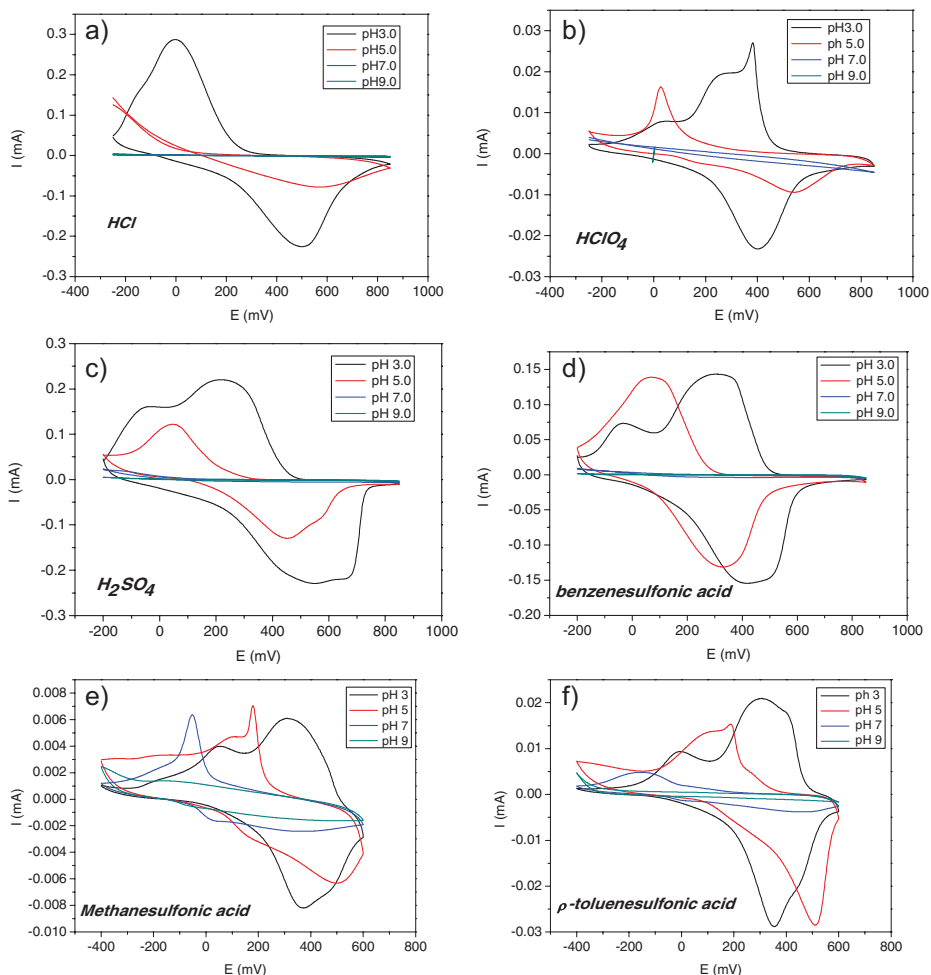


Figure 2.

(a) Cyclic voltammograms GC electrodes modified of (a) PANI (HA), (b) PANI (PA), (c) PANI (SA), (d) PANI (BSA), (e) PANI (MSA), (f) PANI (TSA) films in buffer pH 3.0, 5.0, 7.0, 9.0.

of the peak heights, and a shift of the peaks takes place. This reveals that during the dedoping process small anions can be released from PANI films, and the protons that are not electro statically retained by the small anion scan diffuse out of the polymer network into the buffered solution.

In pH3, PANI doped with SA gave the highest redox current. Compared with the other acids, each SA molecule can release two protons. This indicates that as more protons are available in the PANI polymerization, its growth will be faster. How-

ever, researchers have found that a fast growth rate gives rise to more irregular of the PANI structure and decreases the polymer conductivity.^[28] This conclusion was confirmed by our results as the redox peak current in the PANI (SA) films decreased most clearly when the pH value of the solution was increased. Adversely, the growth rates of PANI doped with MSA and TSA were slower. MSA and TSA have a more hydrophobic structure than SA and BSA protecting against the pH change. The more hydrophobic the dopant is, slower polymerization rate is.^[29]

An interesting phenomenon was that the oxidation peaks of PANI (SA) and PANI (BSA) moved towards the electronegative potential at pH 5 although with PANI (MSA) and PANI (TSA) shifts toward more electropositive potential were observed. This is probably a result of the hydrophobic environment limiting the diffusion process. In general, we suspect that association capability of the counter ion is an important factor in the acid diffusion away from the PANI films.

Effect of Polyelectrolytes

Since the large anions (polyelectrolyte) are not able to leave the polymer matrix due to the entanglements originated during the polymerization process, the large counter ion interactions with the cationic PANI chain can result as a stable polymer matrix. PANI films complexed with large anions

have been intensively reported. However, many polyelectrolytes, like polyacrylic acids, have had weak charges, thus is not enough to compensate all the cationic sites on the oxidized PANI chain.^[30] Therefore, it is necessary to use acidic macromolecules as electrolytes during PANI synthesis. Here, we chose HA, PA and SA as the electrolytes in the polymerization of PANI in the presence of PVSA. Figure 3 presents the relationship between the pH sensitivity and the electrolyte. Higher pH sensitivity is observed for the PANI film prepared from SA solution (Figure 3c). Although the effect of the acid electrolyte is not very remarkable, we can speculate that the reason is related to their molecular structure. The exchange of chloride and chlorate ions is easier in the presence of the sulfonic acid groups, and therefore the stability of the films was increased. This confirms that the pH behavior of PANI strongly depends on the type of electrolyte.

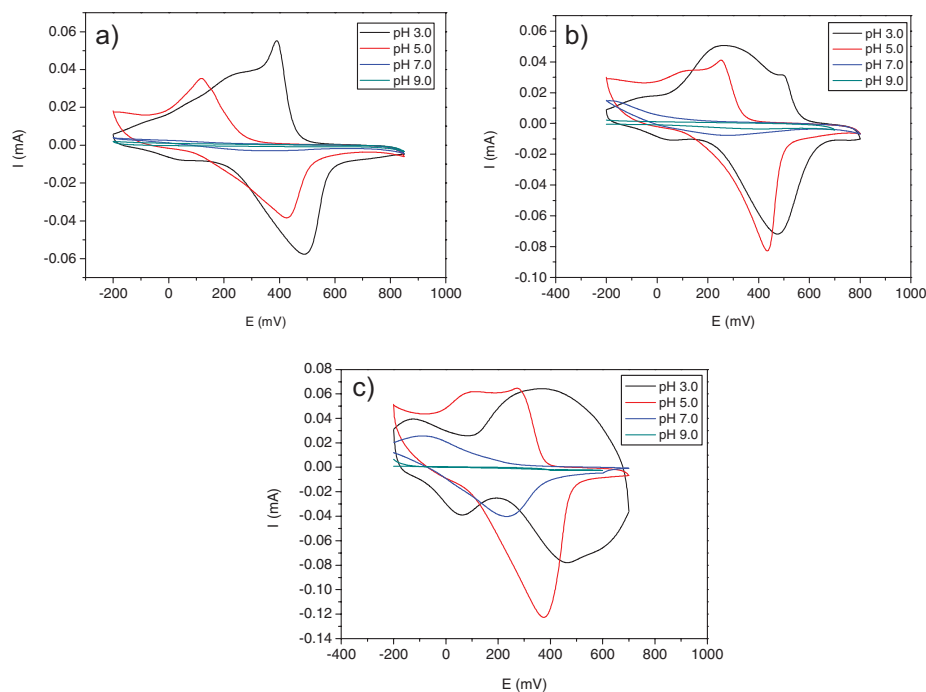


Figure 3. CVs of PANI coated GC electrodes in pH 3, 5, 7, 9. PANI (PVSA) films polymerized in the presence of (a) 1M HClO_4 , (b) 1M HCl , (c) 1M H_2SO_4 as electrolyte.

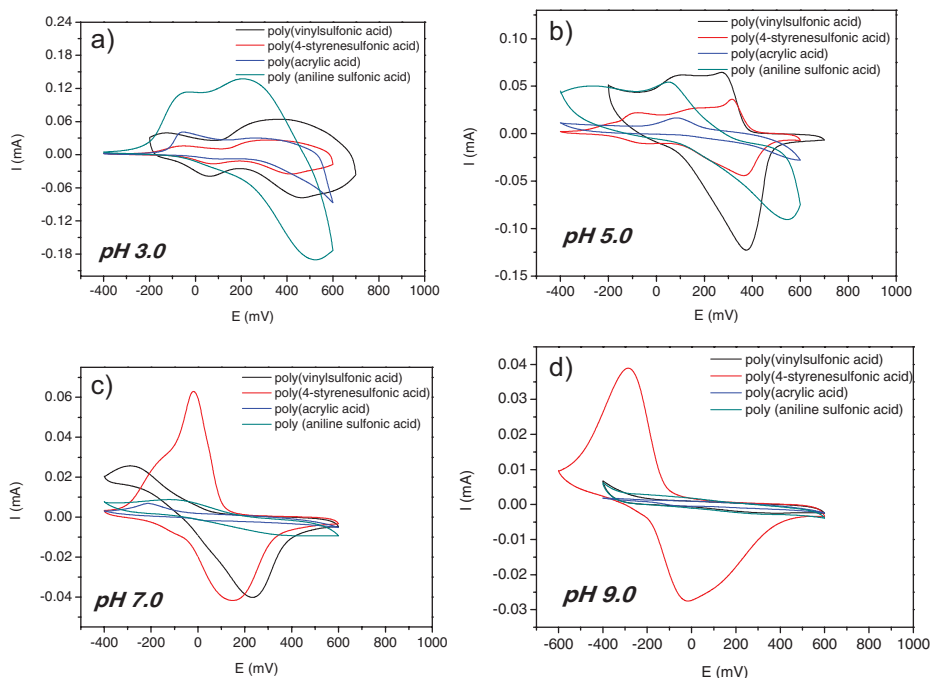


Figure 4.

Cyclic voltammogram GC electrodes modified of PANI (PVSA), PANI (PSSA), PANI (PAA), PANI (PVSA) films in buffer (a) pH 3.0, (b) pH 5.0, (c) pH 7.0 and (d) 9.0.

Effect of Large Counter Ion dopants

Figure 4 shows the pH sensitivity behavior of PANI polymerized with different polymers. It can be seen that the anodic and cathodic peaks are higher than those of the PANI films doped with small anions. This confirmed that polyelectrolyte can retain PANI's stability even at higher pH values. But different polyelectrolyte also showed different behavior. PAA is the weakest acid among these polymers and therefore the redox currents are smaller than those for the others. PASA showed similar behavior with sulfuric acid; the high growth rate gives rise to the irregular PANI structure and quick degradation in higher pH values. The only one dopant which can retain PANI electro active in pH 7 solution is PSSA. From Figure 4, it is obvious that there is only a small current difference between pH 3 and pH 7, indicating that the PSS counter ion retains protons more effec-

tively than PVSA. The binding between PANI and PSSA could be mainly due to the hydrophobic interaction between the aromatic group in the polymer anion and the anilinium ions.^[31] These results ensure that PSSA could be possibly used as dopant for PANI to effectively maintain the inherent electroactivity of PANI in the neutral media. We tested the stability of PANI films doped with PSSA in pH 7.0 buffer for two days, the cyclic voltammograms showing the redox activity of PANI were almost the same before and after the experiments.

Effect of Immobilization Method

The redox behaviors of PANI modified on GC electrode by layer-by-layer assembly in different pH solution are shown in Figure 5. The CVs of PANI films exhibit two resolved pairs of redox peaks at acidic pH (pH 3), as was observed using

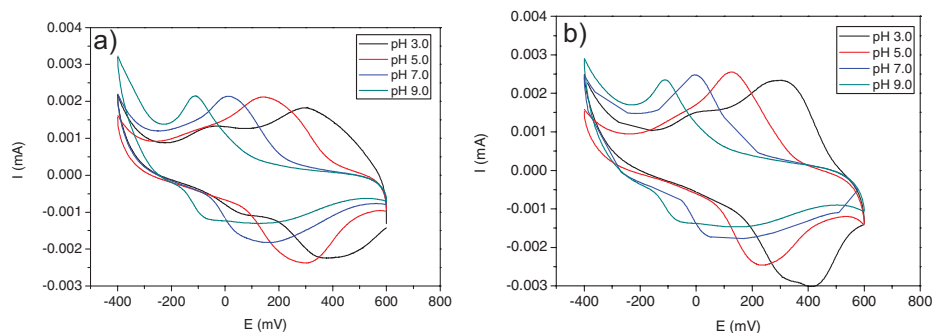


Figure 5.

CVs of (a) PANI/PSSA and (b) PANI/PAA layer by layer modified electrodes in buffer pH 3.0, 5.0, 7.0 and 9.0.

electrodepositing method. But with electrodeposition only, as the pH increased, the corresponding redox peaks shifted to more negative potential and overlapped to produce the single pair of peak. For layer-by-layer method, the cathodic peak current changed with small steps with the pH increasing, and the anodic peak currents decreased even less. This behavior is due to the formation of a complexes (an adherent and compact passive film) hindering the redox processes of the PANI films and thus, the decrease of the anodic oxidation current takes place. On the other hand, the cathodic reduction peak appears in the same potential range, but in this case, it is narrower and higher.^[32] And when PANI films are deposited with negative polyelectrolyte layer-by-layer deposition, the negatively charged polyelectrolyte deposited on top of each layer. Thus the polyelectrolyte may block the dedoping process of PANI, and resulting films maintain the electro activity at neutral pH.

Conclusion

In summary, we report herein the electro polymerization of aniline with different types of dopants. A comprehensive study regarding the electrical properties of a series of PANI films in different pH's has been performed. Our results show that the choice of counter ion, electrolyte and immobilization method has a significant

effect on the polymer growth rate and redox behavior. Large macromolecular counter ions have a stronger stabilizing effect than the smaller ions have. Among these dopants, PSSA is the only one dopant that can effectively maintain the inherent electro activity of PANI in the neutral and alkaline media. This finding is important when using PANI in buffer solutions for monitoring biological binding processes.

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