

New Aspects of Polyaniline Doping: A Study Based on Using Electrochemical Quartz Crystal Nanobalance

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Received 13 February 2006; accepted 24 January 2007

ABSTRACT

Oxidative and non-oxidative dopings of polyaniline in various acidic media with different concentrations have been studied by electrochemical quartz crystal nanobalance technique. Polyaniline was synthesized electrochemically on the gold electrode of quartz crystal using a galvanostatic electropolymerization method (1 mA/cm²). Electrochemically synthesized polyaniline film was exposed to different concentrations of various acidic solutions and the changes in the mass (frequency) of the polymer were recorded. Results showed that the extent and the rate of non-oxidative doping depend on the concentration and nature of dopant acid. The rate of doping in the case of a number of tested inorganic acids was as the order of: H₃PO₄<HCl<HClO₄<H₂SO₄. Exposure of doped polyaniline to ammonia solution (0.5 M) resulted a mass reduction in the polymer film due to the non-oxidative undoping process. Further experiments showed that this doping/undoping behaviour is a completely reversible process. Mass changes of the polymer in oxidative doping/undoping process were also recorded. It was also found that at pH values lower than 1, the total mass change during oxidation of the polymer was dependent on acid (or proton) concentration. However, at pH values over 1, the mass change during oxidation was independent of acid (or proton) concentration. These two observations support two different mechanisms of doping suggested by other workers.

Key Words:

polyaniline;
ion transport;
electrochemical quartz crystal
nanobalance;
conducting polymers;
doping.

INTRODUCTION

Electrically conducting polymers are an important and interesting class of new organic materials that have gained considerable attention in the recent years. These polymers have been used in many applications including sensors [1,2], switchable membranes [3], anti-corrosive coatings [4,5], biosensors

[6], electrochromic devices [7], and rechargeable batteries [8,9]. Most of the works, in this area, are focused on the dynamic reversible redox properties of the polymers.

Polyaniline is one of the most important classes of conducting polymers that has been studied extensively [10,11].

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Polyaniline can be doped and undoped on exposure to an acidic or alkaline environment without changing the number of π -electrons in the polymer [12]. This mechanism is attributed due to the presence of NH and N groups in the polymer backbone whose protonation and deprotonation will bring about a change in the electronic conductivity as well as in the colour of the polymer [13]. It is believed that all or some of the nitrogen atoms (amines or imines) in any species can be protonated with protonic acids [14]. This aspect of doping and undoping makes polyaniline and its analogous highly suitable for industrial applications. Various organic and inorganic acids and salts can dope polyaniline [15-18]. Protonation/doping of polyaniline by acids may be carried out during polymerization of aniline in the presence of acids in polymerization solution [18-21] or after polymerization by holding the polymer in an acid solution [22-24]. The protonation degree of amine and imine sites in polyaniline depends on the type and concentration of acid solution [25,26]. The behaviour of insertion or exertion of cations and anions after protonation depends on the kind, size and activity of ions and the structure of the polymer [27,28]. On the other hand, the degree of polyaniline protonation is effective on its structure, conductivity and electroactive properties which are important in applications of polyaniline in various fields [29-35].

The polymer can be also doped by partial oxidation/reduction of the polymer chain (oxidative doping) [12]. The redox reactions of conducting polymers are accompanied by mass exchanges as ion migration into or out of the polymer film. Therefore, the weight changes of the polymer films during the redox reactions can give us information concerning the reaction mechanism. There are several ex-situ measurements of ion content of the polymer following the redox reaction [12,36]. But, it has been recently knowledged that the doping-undoping processes that occur upon oxidation/reduction of conducting polymers are not as simple as being described at the early stage of their discoveries [37]. It is a complex behaviour of distinct anion and cation transport processes that occur at the solid state polymeric electrode/solution interface during the redox reaction. There is a need to an online/real time technique for in-situ monitoring of what happens during the redox reactions or doping-

undoping processes of conducting polymers.

Using the electrochemical quartz crystal nanobalance (EQCN) technique, it is possible to study the changes in the mass of thin layers such as polymer films in-situ. The converse piezoelectric effect is the basis of EQCN technique, where application of an electric field across a non-centrosymmetric (acentric) crystal produces a shear strain proportional to the applied potential. This is a low cost piezoelectric technique where small changes in mass (Δm) can be monitored by measuring the oscillation frequency (ΔF) of a quartz crystal according to the well-known Sauerbrey equation [38]:

$$\Delta F = -2f_0^2 \Delta m / A(\mu_g d_g)^{1/2} \quad (1)$$

where f_0 is the frequency of a quartz crystal, μ_g is the shear modulus of the quartz, d_g is the density of the quartz, A is the surface area of the quartz plate undergoing oscillation, and Δm is the mass change corresponding to the frequency change (ΔF).

EQCN technique has been extensively used to study the structure and reactions of conducting polymers [39-45]. Some of these works are related to the electrochemical synthesis of polyaniline on the quartz crystal [39,40]. These studies have provided information about the anion or cation insertion into the polymer film during electrochemical growth. In some other works the redox reaction mechanism of polyaniline films have been studied in aqueous and non-aqueous electrolyte solutions [41,42]. Bacskal et al. [43] have studied the effect of electrolyte nature, H^+ -ion activity and film thickness on the degree of protonation of polyaniline films both in their reduced and oxidized states. However, in previous studies the mechanism and kinetics of doping process have not been studied in details.

It has become clear that the electrochemical behaviour of polyaniline films is even more complex than that of other conducting polymer films, because all species of different oxidation states can be expected to be protonated to some extent. In this work we aim to study the redox behaviour of polyaniline using EQCN technique. The mechanism and kinetics of polyaniline oxidative and non-oxidative doping/undoping processes are described in details.

EXPERIMENTAL

Reagents and Materials

Hydrochloric acid, sulphuric acid, phosphoric acid, perchloric acid, and aniline were purchased from Merck chemicals (Germany) and were of analytical grades. All chemicals were used as received, and aniline was distilled prior to use.

Instrumentation

10 MHz AT-Cut quartz crystals with gold electrodes on both sides were commercially obtained from Int. Crystal Manuf. (ICM, Oklahoma, USA). For EQCN experiments a home-made apparatus was used which is described in our previous work [44]. The oscillator circuit used was based on that designed by Bruckenstein and Shay [45]. However, some modifications of the original design were also carried out to improve mass sensitivity and stability [46].

A galvanostat/potentiostat Wenking TG 97 from Bank (Germany) and a pH-metre 654 from Metrohm (CH 9101-Herisau, Switzerland) were used for the synthesis of the polymer. A three-electrode system consisted of a gold working electrode on quartz crystal, a platinum gauze as auxiliary electrode and Ag/AgCl as reference electrode was used for polymer synthesis and electrochemical experiments.

Polymer Synthesis

Polyaniline was synthesized electrochemically on gold electrode of quartz crystal wafer. A solution containing 1 M aniline and 2 M HCl was used for electropolymerization. In a galvanostatic electropolymerization, a constant current density of 1 mA/cm² was applied to the working gold quartz crystal electrode. During electropolymerization, frequency shift of quartz crystal electrode was recorded. Also during galvanostatic polymerization the potential of working electrode was recorded against time.

RESULTS AND DISCUSSION

Polyaniline was synthesized on gold electrode of one side of the quartz crystal electrode using galvanostatic electropolymerization method (1 mA/cm²). Change in the frequency of the crystal was recorded during

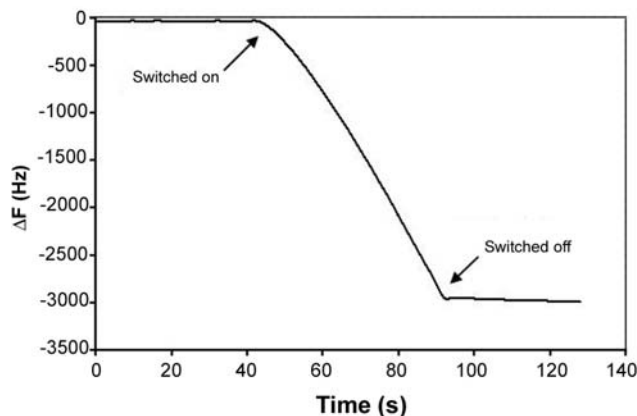


Figure 1. Frequency changes of the quartz crystal during electropolymerization of aniline at the surface of quartz electrode by a constant current density of 1 mA/cm².

electropolymerization (Figure 1). Frequency of the crystal was decreased during electropolymerization due to the increasing of polymer mass on the crystal.

In order to apply Sauerbrey equation (eqn (1)) to these frequency changes of the crystal, the assumption was made that the acoustic properties of the foreign layer were identical to those of the quartz. This assumption is valid only if a rigid material is deposited on the crystal. It was shown that the polymer films can be treated as rigid and free from elastomeric effects if a linear response of frequency with time (or charge) is observed during electrodeposition [40].

As it can be observed from Figure 1, there is a linear relationship between the time of electropolymerization and the frequency changes of the quartz

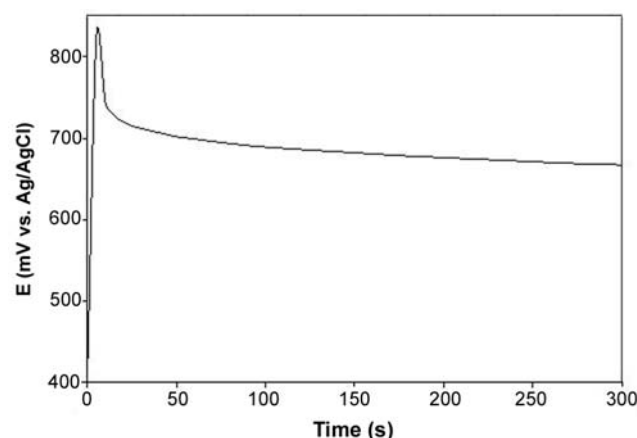


Figure 2. Chronopotentiogram for the galvanostatic electropolymerization of aniline at the surface of quartz electrode by constant current density of 1 mA/cm² in an aqueous solution of 1 M aniline and 2 M HCl.

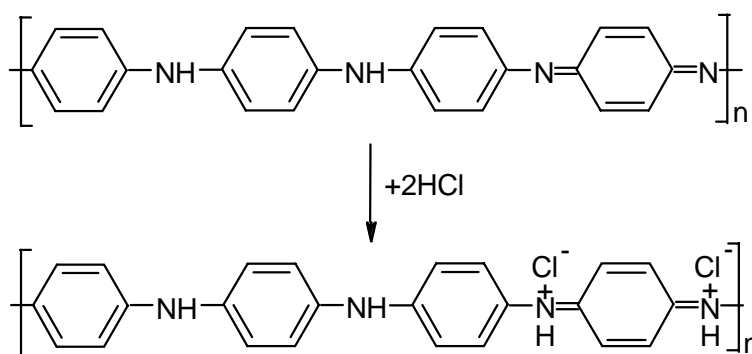
crystal during galvanostatic electropolymerization ($R^2=0.995$). This indicates that the polymer could be treated as rigid and free of viscoelastic effects and validates the use of Saurebrey equation to convert frequency data to mass changes. Therefore, mass changes calculated from the data in Figure 1 was 2850 ng for polymer growth on the crystal.

Potential of the quartz crystal during galvanostatic electropolymerization of aniline was also recorded against time (Figure 2). The decrease in potential indicates the deposition of a conducting layer on electrode and increasing the rate of cation radicals production during the growth of polymer chains.

Non-oxidative Doping

The Effect of Concentration of Dopant

In order to investigate the non-oxidative process of polyaniline doping, the prepared polyaniline on the quartz crystal electrode was exposed to various concentrations of aqueous HCl solutions and the relevant mass change was measured (Figure 3).



Scheme I

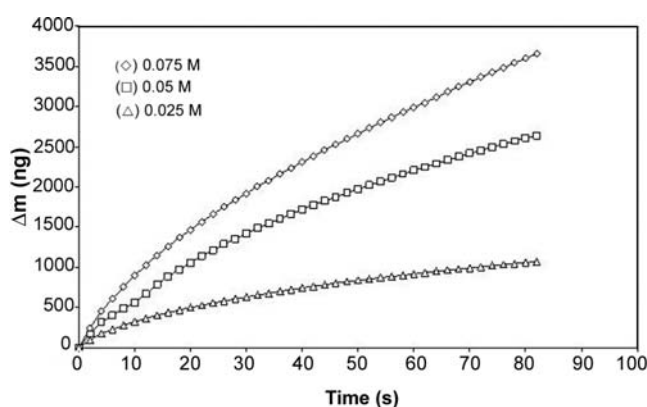


Figure 3. Mass changes of the polyaniline film on the quartz crystal electrode upon exposure to various concentrations of aqueous HCl solutions.

It was found that as the acid concentration increased, more dopant ions penetrated inside the polymer and increasing changes occurred in the mass.

On the other hand, as the concentration of dopant acid increased, the rate of doping increased as well. The reaction occurring can be explained by Scheme I. This assumed that with more acids more nitrogen atom sites were protonated and as a result, the rate of doping increased.

The Effect of Nature of Dopant

The polyaniline synthesized on the gold electrode of the quartz crystal was exposed to 0.05 M of various acid solutions (H_3PO_4 , $HClO_4$, H_2SO_4 , HCl) as dopants. The rate of doping in each case was measured (Figure 4). The slope of each curve in this figure shows the rate of the doping by the relevant acidic dopant. According to the results, the following order for the rate of polyaniline doping by various acidic solutions was obtained:

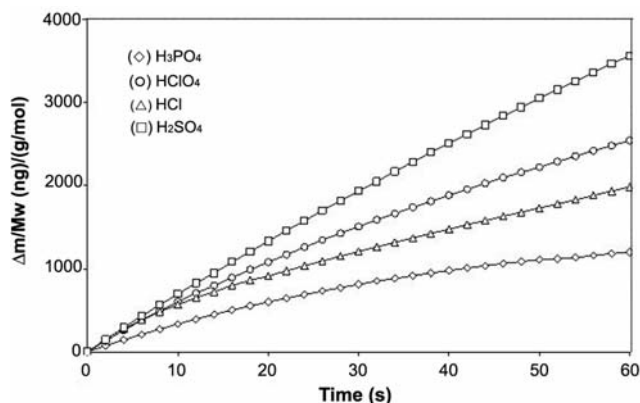
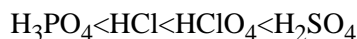


Figure 4. Mass changes of the polyaniline film on the quartz crystal electrode upon exposure to aqueous solutions of different acids with the same concentration of 0.05 M.

This indicates that the ability of each acid to dope polyaniline depends on its nature and ionic strength. The results show that the rate of doping does not depend only on anion concentration but on its nature as well. It should be noted that the total mass change for each acid was normalized against molecular weight of its relevant dopant.

Reversibility of Non-oxidative Doping

In order to study the reversibility of non-oxidative doping process of polyaniline by acidic solutions further experiments were carried out. The polyaniline synthesized on a quartz crystal was exposed to various acid solutions (H_3PO_4 , $HClO_4$, H_2SO_4 , HCl) with the same concentration of 0.05 M. Changes in the frequency of the quartz crystal indicated increase in the mass of the polymer film due to the non-oxidative doping process in contact with acidic solutions (Figure 5). In between each doping process by various acids, the doped polymer was exposed to an ammonia solution of 0.5 M concentration and the relative mass change was recorded (Figure 5). It was found that upon exposure to ammonia solution, polymer mass decreased indicating that the polymer was undoped by ammonia solution. Back shift of the mass change to its initial value (before contact with acid solution) means that the non-oxidative doping in polyaniline is a completely reversible process. On the other hand, the reaction shown by Scheme I is a reversible reaction.

Oxidative Doping

The galvanostatically synthesized polyaniline was subjected to a cyclic voltammetric method in an aque-

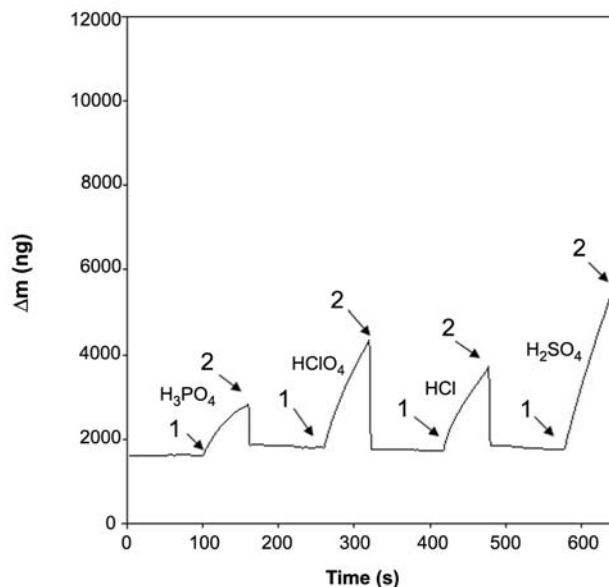
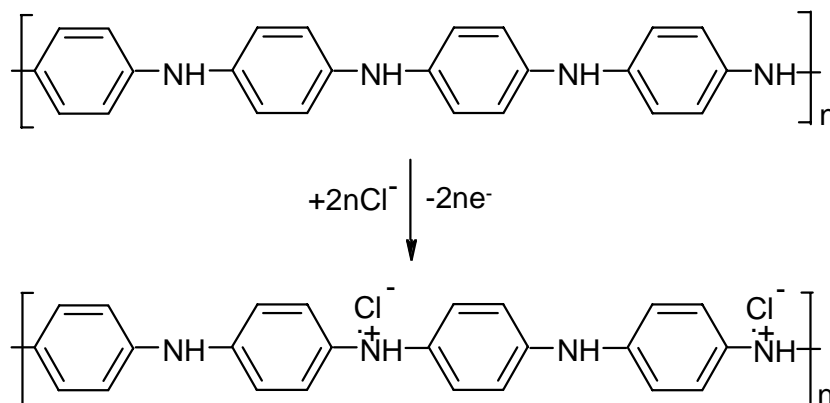


Figure 5. Non-oxidative doping/undoping process in polyaniline: (1) upon exposure to acidic solution; and (2) upon exposure to ammonia solution.

ous media containing 0.5 M HCl . The relevant change in the mass of the polymer film (massogram) and its cyclic voltamogram was recorded (Figure 6). It was found that the polymer mass increased upon oxidation and decreased upon reduction in a reproducible manner. The reaction taking place can be justified using Scheme II.

The fully reduced form of polyaniline (leucoemeraldine) is oxidized to emeraldine when an oxidative potential is applied. This is a process in which electrons are removed from the polymer backbone during oxidation followed by inward diffusion of anions into the polymer to neutralize the positive sites created during the oxidation process. Electron



Scheme II

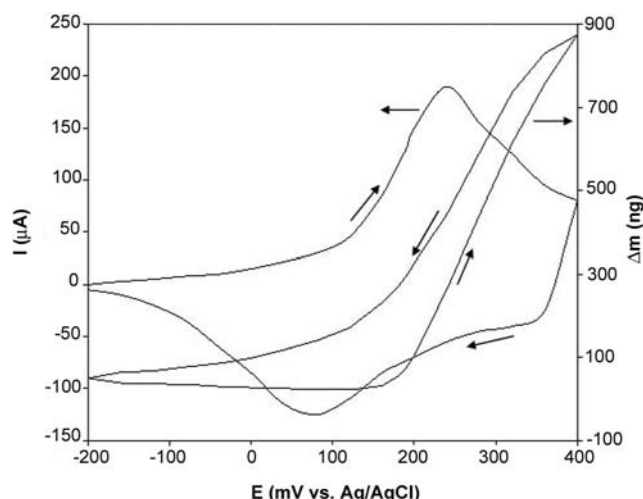


Figure 6. In-situ cyclic voltammogram and massogram (quartz crystal nanobalance response) during oxidative doping of polyaniline in a 0.5 M HCl solution with a scan rate of 4 mV/s.

uptake during the reduction period converts it from a positive to neutral form, resulting to the exertion of inserted anions out of the polymer film. This results to the mass decrease in polymer backbone. As it is observed from Figure 6, mass changes of the polymer during oxidation and reduction processes are occurred in a reversible manner. In other word, the oxidative doping of polyaniline is a reversible process.

The effect of oxidative-reaction was further investigated in the presence of different dopants (Figure 7). A similar trend was observed as non-oxidative doping with expectation of H_3PO_4 . With 0.25 M dopants, pH value remained above 1. The anions participated in doping process (Scheme II) and relative mass change

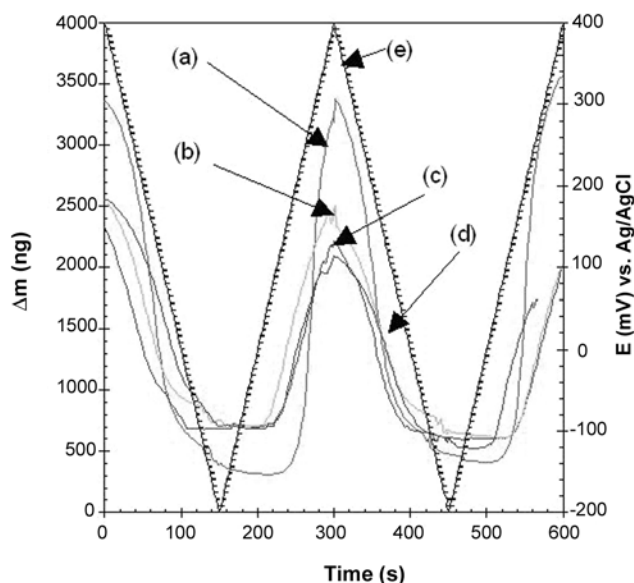
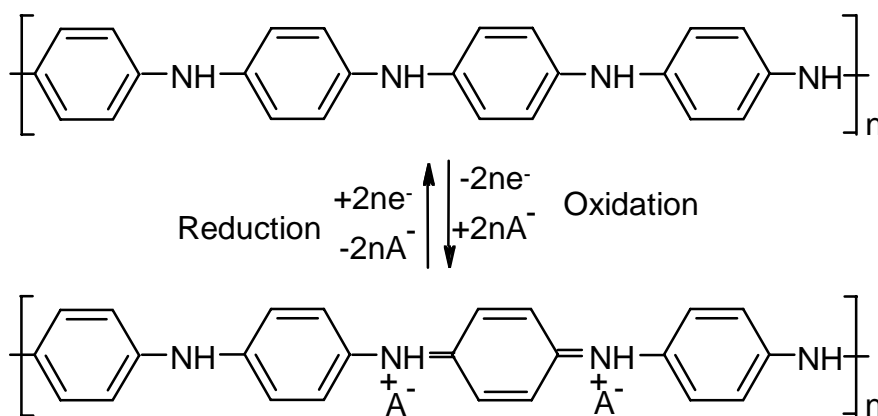


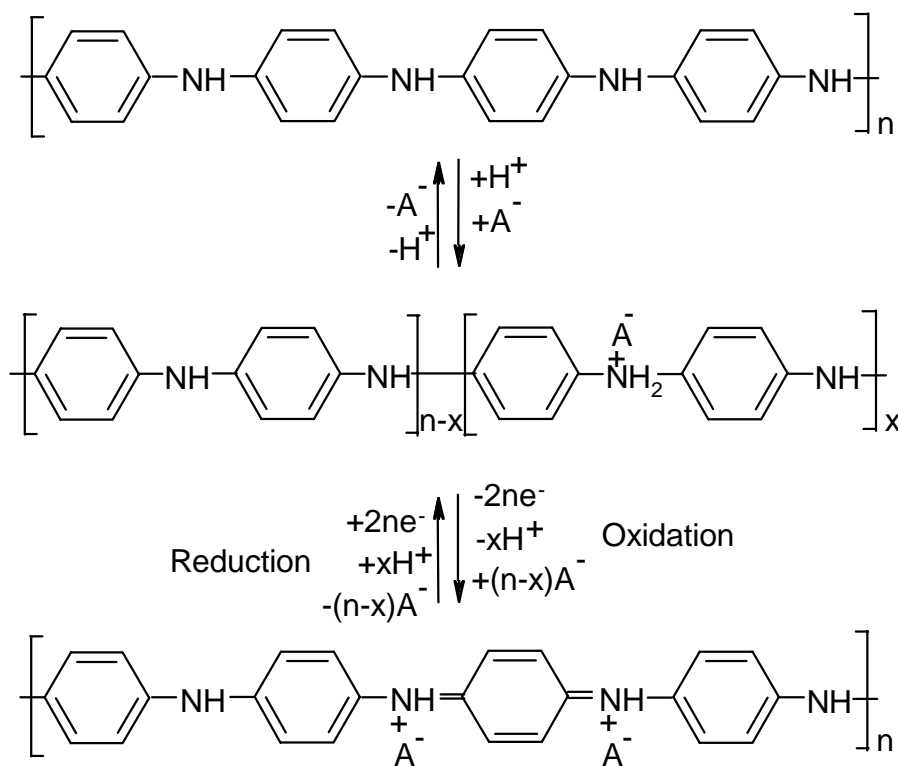
Figure 7. Mass changes of the polyaniline film on the quartz crystal electrode during oxidative doping in different acidic solutions: (a) 0.25 M H_3PO_4 ; (b) 0.25 M HCl; (c) 0.25 M HClO_4 ; (d) 0.25 M H_2SO_4 ; and (e) voltage, scan rate = 4 mV/s.

was observed. The nature of anions played an important role in mass change value and therefore various amounts of mass change were observed (Figure 7). The results indicate that the oxidative doping is also an anion dependent process.

In order to determine the different behaviours observed for H_3PO_4 , more investigations were carried out. The effect of dopant concentration (H_3PO_4) was investigated during oxidative doping of polyaniline (Figure 8). The total value of mass change that occurred during oxidation of polymer (Figure 8) was



Scheme III



Scheme IV

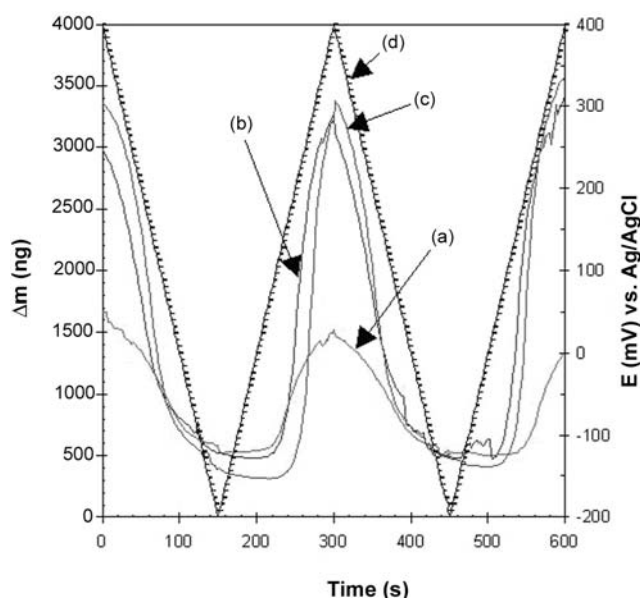


Figure 8. Mass changes of the polyaniline film on the quartz crystal electrode during oxidative doping in various concentrations of aqueous H_3PO_4 solutions: (a) 1 M; (b) 0.5 M; (c) 0.25 M; and (d) voltage, scan rate = 4 mV/s.

almost equal for the different concentrations of the acid (0.25 M and 0.5 M). It means that protons did not

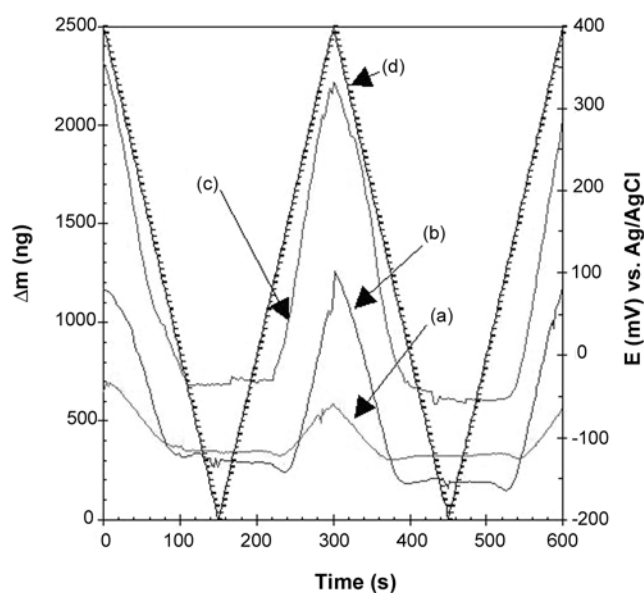


Figure 9. Mass changes of the polyaniline film on the quartz crystal electrode during oxidative doping in various concentrations of aqueous $HClO_4$ solutions: (a) 1 M; (b) 0.5 M; (c) 0.25 M; and (d) voltage, scan rate = 4 mV/s.

participate during redox reaction and the process occurred with dominant role of anions. In such a con-

dition pH values were over 1.

When the pH value was lower than 1 (Figure 8a), the proton role was dominant in the doping process and less mass change was observed while polymer oxidized. Such a behaviour was not observed in the case of HClO₄ as in a concentrate solution (1 M) pH value was over 1 (Figure 9). It seems that at pH values over 1, nitrogen sites are not protonated and redox process accompanied by dominant role of anions (Scheme III). However, at pH values lower than 1, more nitrogen sites are protonated and redox process is accompanied by dominant role of protons with much less contribution from anions (Scheme IV).

We can conclude that by increasing proton concentration, more nitrogen sites are protonated and therefore, less anions are participated during redox reactions, as evidenced by EQCN results. Other workers have also shown that at pH values over 1, the redox reactions are independent of proton concentration [47]. Our results are in agreement with previous works.

CONCLUSION

Using variety of measurements, it was found that the non-oxidative doping in polyaniline is a time dependent process. The rate of doping is influenced by the nature of acid employed. In the case of H₂SO₄ the highest rate of doping was obtained (H₃PO₄<HCl<HClO₄<H₂SO₄). However, the oxidative doping was quick enough to be independent of kinetic effects. The effect of acid concentration was also studied with respect to the rate of doping. At pH values lower than 1, the total mass increase during oxidation of the polymer was varied depending on acid (or proton) concentration. However, at pH values over 1, the mass change occurred during oxidation was independent of acid (or proton) concentration. These observations support two different mechanisms of oxidative doping in polyaniline.

ACKNOWLEDGEMENTS

We are most grateful for the continuing financial support of this research project by the University of Tabriz.

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