In situ measurement of pH in the interior of conducting polymer microtubules

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Abstract

Visible spectral absorption studies of an indicator trapped in the microenvironment of polypyrrole (PPY) and polyaniline (PANI) films were used to investigate the change in pH accompanying changes in oxidation state of the polymer. An indicator, bromophenol blue was incorporated in the conducting polymer film during the electropolymerization process. In situ UV-vis spectra of these films were recorded in aqueous solution of KCl. The results obtained show that with increasing potential of the film, the pH of the microenvironment decreases both for PPY and PANI. The change in pH is greater in the potential range where the change in electronic conductivity is also greater.

Keywords: Polypyrrole; Polyaniline; Bromophenol blue; pH

1. Introduction

Polypyrrole (PPY) and polyaniline (PANI) are two of the best-known conducting polymers, and have been intensively studied as electroactive material for several years [1–4]. Because of their various important applications in batteries [5–7], gas separating membranes [8,9], sensors [10–13], microelectronic devices [14], various coatings [15,16] and composite materials [17,18], conducting polymers have generated wide spread interest as potential materials of choice. They have interesting optical, mechanical and electrical properties because of which it is possible to use them in situations where inorganic materials are not suitable. The most prominent feature of these materials is an ability to be charged and discharged during potential variation. This electrochemical doping and undoping involves the ion exchange with the solution.

Ion transport in conducting polymers was studied by different analytical techniques such as X-ray photoelectron spectroscopy [19–21], scanning electrochemical

microscopy [22], luminescence [23,24], electrochemical quartz crystal microgravimetry [21,25–30], rotating ring-disk voltammetry [31,32]. For PPY the dominant ionic species depends on the choice of the dopant anion and the solvent/electrolyte system [33,34]. It has been known that anion transport is dominant in the film doped with a small size anion such as PPY/nitrate (PPY/NO₃) [35], PPY/chloride (PPY/Cl) [21], and PPY/perchlorate (PPY/ClO₄) [36] films. But it has been also reported that H⁺ and OH[−] ions are involved in ion transport during the redox reaction of PPY films with small counter anions [21,37]. In some cases pH changes near the polymer film were measured by using a micro-combination pH probe [21,36]. A spectroelectrochemical study of the proton exchange process in the electrochemical reaction of PPY using a pH indicator in electrolyte solution was first reported by Tsai et al. [38]. Okano et al. [39] in 1985 showed an increase in pH of the bulk solution for a positive scan of the PPY electrode, whereas Tsai et al. reported a decrease in pH with increasing potential. As ion exchange with the solution is a diffusion-controlled process, the chemical potential and pH of the microenvironment could be different from that of the bulk. In the case of PANI, MacDiarmid and co-workers have proposed proton exchange at pH −0.2 to −2.1 and anion exchange

between pH 1–4 as the predominant processes [40]. Kobayashi et al. [41] proposed a model in which the reduced PANI is protonated at pH < 4 and protons are exchanged at potentials below 0.45 V whereas anion insertion was dominant at higher potentials. Shimazu et al. [42] have studied in situ proton exchange in and out of the film at different pHs (−0.3 to 3) using a long optical path length thin layer cell (LOPTLC) combined with an ion selective FET sensor. Various acid base indicators of low concentrations were added to the electrolyte to monitor the change in proton concentration in the pH range −0.3 to 3 spectroscopically. Their results indicate that exchange of protons for charge neutralization is predominant mainly at pH ≤ 2. At pH ≥ 3 anion transfer is predominant though some proton exchange occurs at pH 3 also. Till pH 3–4 the reduced form seems to be protonated. But at high pH the reduced form is completely deprotonated and so anions must be injected upon oxidation for charge neutralization. Lapkowski and Genies have also used a pH indicator in electrolyte solution to study the mechanism of proton exchange accompanying the electrode reactions of PANI [43]. Conductivity of these polymers is very sensitive to the chemical potential and pH of the microenvironment within the polymer matrix and this concept is used to design biosensors. In order to understand how the redox process and conductivity changes with the change in pH of the microenvironment, it is important to measure the pH of the interior of the film independently. In the present study we have incorporated dye molecules during the process of electropolymerization and in situ pH changes within the microenvironment were observed.

2. Experimental

In situ UV–vis spectra were recorded for a conducting polymer film deposited on a gold-coated polycarbonate (PC) isoporous membrane and on ITO glass. The PC membranes were obtained from the Millipore Corporation. The membranes consisted of randomly distributed pores of uniform diameter. Studies were carried out with the membranes having pores of 0.1-μm diameter. The thickness of these membranes was 10 μm. Gold was deposited on one side of the membranes by a 15F6 HINDHIVAC vacuum evaporation system.

Polymer films were electrochemically deposited on the gold-coated PC membrane in a three electrode one-compartment cell having the facility of purging with N₂. A small clip holder having a suitable contact facility held the working electrode. The reference electrode was SCE and a platinum foil was used as the counter electrode. For the synthesis of PPY before starting polymerization N₂ was passed through the monomer solution (0.1-M pyrrole in 0.1 M KCl) for 30 min. PANI was synthesized

from 0.1-M aniline in 0.5 M H₂SO₄ solution. Polymerization was carried out by a potentiodynamic method. The potential range used for PPY was 0.0–1.0 V and for PANI it was −0.2 to +0.8 V vs. SCE at 50 mV s^{−1}. The thickness of the film was controlled by the number of cycles of potentiodynamic polymerization. Polymer films containing the indicator, bromophenol blue (BPB) were deposited in the same way after adding the required amount of BPB to the monomer solution. In the case of PANI, the amount of BPB adsorbed during electropolymerization was small. Therefore, after polymerization the film was kept in the pH 3 solution containing BPB for around 1 h to allow the indicator to be immobilized on the surface of the polymer.

The films were washed after synthesis and in situ absorption spectra were recorded in aqueous KCl solution. The quartz cells for spectral studies had a 1-mm optical path length for use with the polymer-coated membrane. While recording the in situ spectra of polymer films, the potential was applied through the use of platinum wire to connect the film and the counter electrode. Ag/AgCl wire was used as the reference electrode. In situ absorption spectra were recorded with a Shimadzu UV–vis recording spectrophotometer (UV-2100). The potential was controlled by an EG&G model 362 potentiostat.

Cyclic voltammograms were obtained by using a Linseis LY 16100 XYt recorder connected to the potentiostat. In situ resistance measurement of the polymer film was carried out using a PINE AFRDE4 bipotentiostat.

Distilled pyrrole and aniline were used to prepare monomer solutions. The monomer solutions were kept refrigerated and under a nitrogen atmosphere. Colourless monomer solutions were used for all the experiments. Water purified by the Milli-Q system was used to prepare all the solutions.

3. Results and discussion

Spectroelectrochemical studies of polymer films were performed using PC membranes as well as ITO-coated glass. For both cases we obtained similar absorption spectra. A polymer film on a porous PC membrane has polymer microtubules inside the pores of the membrane; therefore the spectra obtained are for polymers with microtubular structures. We were interested in knowing the pH change inside the conducting polymer microtubules as they have been used to fabricate biosensors and biosensor arrays [44]. It has also been reported that these conducting polymer microtubules have good transducing abilities as their conductivity depends strongly on their electrochemical potential states [45].

The electrochemical characteristics of conducting polymer films and those containing BPB can be deduced

from the cyclic voltammetric measurements. During electrochemical polymerization, the BPB molecules become trapped in the polymer matrix. A monomer solution with $\leq 8 \times 10^{-4}$ M BPB, gives a polymer film containing BPB, which shows a similar CV to the pure polymer film. In the presence of higher than the above BPB concentration, we observed a slight change in the CV. In general for a lower concentration of BPB, both voltammograms exhibit redox features characteristic of the corresponding polymer film. Overall, the shapes of the cyclic voltammograms indicate that there is no change in the redox processes after immobilizing BPB in conducting polymer films using a small amount of BPB in the monomer solution. Therefore all further experiments were carried out using $< 8 \times 10^{-4}$ M BPB in monomer solution.

Conductivity measurements were carried out for both types of film at pH 3 and at pH > 5. Conducting polymer films containing BPB show a type of conductivity change with potential similar to their respective polymer films. Fig. 1 shows the conductivity behaviour of both PPY and PANI films with the corresponding PPY+BPB and PANI+BPB films at pH 3. With increasing potential, oxidation of the conducting polymer chain takes place and the formation of interband polaronic levels increases the conductance of the film.

From the electrochemical characterization it is clear that the presence of BPB in the microenvironment does not affect the redox process of the polymer film. The leaching of BPB from the polymer films was checked by monitoring the spectra of BPB-containing polymer films with time and it was observed that the absorbance for BPB starts decreasing after only 1 day. Therefore the change in pH of the microenvironment can be measured by taking the absorption spectra at different states of oxidation of the film containing BPB in its microenvironment.

Fig. 1. Plot of log conductance vs. potential for PPY and PANI with corresponding films containing BPB in pH 3 KCl solution.

BPB ($C_{19}H_{10}Br_4S$) is an acid base indicator. It shows two peaks, one at 436 nm, for the acid form of the indicator and the other at 591 nm, for the basic form. With increase in pH the basic peak at 591 nm increases and the peak at 436 nm shows a decrease (Fig. 2).

When BPB was incorporated in the conducting polymer film we could easily monitor the absorption peak for the basic form of the indicator. However the absorption for the acid form at 436 nm merges with the broad absorption peak of PPY around 400 nm. Also, for PANI, the 436-nm peak of the indicator overlaps with that of 440-nm band of PANI and both of these show an increase with increase in potential. Therefore all the calculations for pH change in our case were carried out by monitoring the change in the absorption of the basic peak of the indicator. The indicator absorption at different potentials can be obtained after subtracting the absorption of the corresponding polymer at these potentials.

Fig. 3 shows the absorbance of the PPY + BPB film at different potentials. From Fig. 3 we can easily conclude that the pH of the microenvironment decreases with oxidation of the PPY film (pH 3) as the absorption of the basic form decreases with increasing potential. Though the absorption for the $\pi-\pi^*$ transition of PPY at 400 nm decreases with increasing potential, the change in absorption for the peak at around 400 nm can be explained by the increase of absorption for the acid form of the indicator with increasing potential. With reduction of the oxidized film we observed an increased pH of the microenvironment. The change in absorption at different wavelengths, is very similar for increasing and decreasing potential steps, with a hysteresis in the regions where BPB absorbs. In the same way we have monitored the change in absorbance of BPB loaded in PANI film to calculate the pH change in the microenvironment.

The change of the pH in the microenvironment of the polymer was calculated by considering the following assumptions. (A) The thickness of the polymer film is considered to be 1 μ m. (B) It is assumed that the pH of

Fig. 2. Absorption spectra of BPB with increasing pH: (a) 1; (b) 3; (c) 4; (d) 6 and (e) 8.

Fig. 3. In situ UV-vis spectra of PPY+BPB in pH 3 (0.001 M HCl and 0.1 M KCl). The dotted lines are the base lines for the absorption of PPY in the wavelength region where the basic form of the indicator absorbs.

the microenvironment is the same as that of the bulk under open circuit conditions. The open circuit potentials of BPB loaded PPY and PANI are around 0.3 and 0.2 V, respectively, vs. SCE. This was further supported by the observation of Shinohara et al. [31]. They measured the pH change near a PPY coated Pt electrode at different potentials by means of a micro pH electrode. They showed that close to 0.25 V vs. Ag/AgCl the pH is same to that of the bulk pH. (C). The molar absorption coefficient (ϵ) for the basic form of the indicator (In^-) is same in aqueous solution as in the polymer matrix.

The molar absorption coefficient (ϵ) for the basic form of the indicator was calculated by taking the absorption of the 592 nm peak for solutions of different concentrations of indicator at pH 3. The calculated value of ϵ of In^- is $5.559 \times 10^6 \text{ mol l}^{-1} \text{ m}^{-1}$, which is very close to the literature value.

Then the concentration of In^- (basic form of the indicator) in the microenvironment was calculated from the absorbance at different potentials.

From the equilibrium shown in Eq. (1) and equilibrium constant K (7.9432×10^{-5}) we can obtain the concentration of H^+ . Taking the total indicator concentration as constant (c) we can write Eq. (2). The concentration of H^+ at open circuit (i.e. $[\text{H}^+]_{\text{op}}$) is taken as 10^{-3} M , therefore at open circuit potential we can write Eq. (3). Solving Eqs. (2) and (3) we can calculate the concentration of protons at a certain potential (x) from Eq. (4).

$$[\text{H}^+]_x = \frac{K(c - [\text{In}^-]_x)}{[\text{In}^-]_x} \quad (2)$$

$$[\text{H}^+]_{\text{op}} = \frac{K(c - [\text{In}^-]_{\text{op}})}{[\text{In}^-]_{\text{op}}} = 10^{-3} \quad (3)$$

$$[\text{H}^+]_x = \frac{K([\text{In}^-]_{\text{op}} - [\text{In}^-]_x) + [\text{In}^-]_{\text{op}}[\text{H}^+]_{\text{op}}}{[\text{In}^-]_x} \quad (4)$$

Fig. 4. Plot of ΔpH vs. potential for in situ pH measurement of PPY and PANI in pH 3 prepared by HCl and 0.1 M KCl.

The values of ΔpH i.e. ($\text{pH}_x - \text{pH}_{\text{op}}$) were plotted against the potentials, as shown in Fig. 4. From the figure we can say that the pH change is greater in the range where we observed a large conductivity change. Though for different trials, the numerical value of the pH change varies slightly, the trend always remains the same. The hysteresis in this curve may be explained by slow diffusion rates of the ions for these two cycles as well as some leaching out of BPB at the higher positive potentials where the polymers are known to have a more open structure.

3.1. Ion exchange in PPY films

Several research group have suggested that there are two types of site for dopant anions in the PPY chain [27,37,46,47]. One of the sites is a traditional doping site, i.e. the positively charged conjugated chain.

At -0.5 V we may consider a partially reduced PPY film [37], which contains a certain amount of protons. Bose et al. have shown that PPY is not permselective even in an aqueous solution of KCl (0.1 M) by QCM studies [21]. During the redox reaction, while Cl^- ion transport between the polymer film and the electrolyte solution is the dominant component, the K^+ and H^+ fluxes are no means negligible. They have also shown that proton transport is important especially at solution pHs less than 4 [21]. So with the reduction of the PPY film, H^+ ions move in the opposite direction to that of Cl^- and so the proton concentration of the microenvironment decreases.

Now with oxidation, the decrease in pH can be explained by the deinsertion of H^+ from the film to the microenvironment. This is supported by the data given in Ref. [21], that some H^+ ions come out from the PPY film at pH 3.2 when the film is oxidized from -0.3 to $+0.3 \text{ V}$. The redox processes of PPY can be described

by Eqs. (5) and (6).

The other doping site till now has not been well defined. According to Li and Qian, it may be a protonated pyrrole unit in the PPY chain where protonation on the β -carbon of the pyrrole unit has been shown [37]. However, the result obtained by Xie et al., with PPY and poly (*N*-methyl pyrrole) ruled out the possibility of contribution of the protonated β -carbons in the redox process of PPY [27]. They discussed deprotonation of the NH moiety of pyrrole subunits in neutral and alkaline solutions. Deprotonation of NH moieties removes the positive charges from the polymer backbone, so it occurs more easily at oxidized than at reduced PPY. So we may consider that, with further oxidation, deprotonation occurs and the protons may be trapped in the microenvironment, so that the pH of the microenvironment decreases (Scheme 1).

Reduction of deprotonated PPY will produce negative charges on nitrogen and then hydrated cation insertion will take place. But ultimately, incorporated cations will be ejected since the negative charges are easily neutralized with protons present in the solutions to give $=\text{C}-\text{NH}-$. These can be shown as in Scheme 2.

In our case, though the bulk pH is 3, Schemes 1 and 2 can explain the change in pH of the microenvironment during oxidation and reduction of PPY. The change in pH does not follow the same path, which can also be explained by Schemes 1 and 2.

We also observed the same trend for the change in the absorption of the basic form of the indicator at the bulk pH > 5 . Practically we could not measure the exact pH of the microenvironment at open circuit potential or at other potentials as the optimum pH range of BPB is 3–4.6. However from the decrease of the basic indicator peak absorbance, it can be stated that, at higher bulk pH, also the pH of the microenvironment decreases with increasing potential. The change in pH in this case can be explained similarly as for pH 3. On the other hand, the pH change of the microenvironment can also be

Scheme 1.

Scheme 2.

explained in terms of OH^- insertion and deinsertion. In aqueous solution, oxidized PPY film contains a certain amount of water, and reduction of the film can be shown by Eq. (7) [38].

Yang and Kwak showed that OH^- transport is important during the redox reaction of PPY/Cl films in 0.5 M BaCl_2 solution [28]. Shinohara et al. also showed electrically controlled ion transfer and pH change near a conducting polymer coated electrode in an aqueous solution containing 0.1 M NaBr [31]. As they described, we may also consider that OH^- ion transfer takes place simultaneously with electrolyte anions into or from the PPY film during the oxidation-reduction process of PPY microtubules at pH > 5 .

In situ pH measurements for a PPY + BPB film coated on ITO glass were also carried out. The CVs recorded show that, like a PPY + BPB film on a PC membrane, in this case also, the polymer CV changed when we used a large amount of BPB in the monomer solution. In the spectral studies we observed the same trend of pH change at pH 3 and also at pH > 5 . So we may conclude that whatever the microstructure of the polymer film, the pH of the microenvironment decreases with increasing potential and vice versa.

3.2. Ion exchange in PANI film

For the case of PANI ion exchange in and out of the polymer film, the need to maintain charge neutrality has been studied by several authors [30,41–43]. During oxidation, radical cation sites are formed on the PANI chains. To fulfil the condition of electroneutrality in the polymer, as discussed previously, the process is associated with the incorporation of anions and expulsion of protons depending on the potential and pH of the

solution. At pH 3, the reduced form of PANI is considered to be in a partially protonated state. The decrease in pH in the microenvironment in the case of PANI can be explained by the expulsion of H^+ ions from the film to the microenvironment in the reverse direction of the flow of anions when the polymer is oxidized from -0.5 to $+0.35$ V. The mechanism can be explained in the same way as for PPY (Eq. (5)). On reduction, deinsertion of the counter anions will take place along with insertion of protons from the microenvironment to the polymer film. The increase in pH at this cycle may be explained by Eq. (6).

At -0.5 V at pH 3, PANI can be considered to be in the so called leucoemeraldine base form, which can also be in several states of protonation as shown by Eq. (8) [43].

Though according to Lapkowski and Genies [43], deprotonation of PANI occurs at higher potentials, $E > +0.35$ V, the observed increase of the acidity in our case can also be explained as follows. On oxidation, the deprotonated state of the leucoemeraldine base will be more favourable and a certain amount of H^+ will be ejected from the PANI film and will become trapped in the microenvironment, thus causing a decrease in pH. Simultaneously, on oxidation, PANI will convert to its polaronic state. On reversing the potential of the reduction, the flow of cathodic current will result in the neutralization of polarons and so absorption of trapped protons of the microenvironment to the polymer backbone will occur. This will cause an increase in the microenvironment pH. This is evident from the increase in the peak at 590 nm on reversing the potential.

The spectra were recorded till the potential 0.35 V. This is because at 0.4 V, a decrease in the 800 nm band is observed and a large blue shift of the band to 600 nm occurs for the absorption spectra of PANI at pH 3 in KCl+HCl. This peak will overlap with the indicator peak and so it is difficult to obtain the absorption due to the indicator at a potential $E > 0.35$ V in the present case.

4. Conclusion

It has been shown that one can measure the pH change in the interior of a polymer film by a spectro-electrochemical method. From our studies we have concluded that proton exchange occurs during the redox

reaction of PPY and PANI even when small counter anions like Cl^- are present in the electrolyte solution.

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