THE RESPONSE OF POLYPYRROLE COATED SOME METALLIC AND GLASSY CARBON ELECTRODES TO HYDRONIUM ION ACTIVITY IN AQUEOUS SOLUTIONS

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abstract: Polypyrrole (PPy) coated Pt, Au and glassy carbon (GC) electrodes as indicator electrodes for hydronium ions (H_3O^+) - *p*H electrodes - in aqueous solutions have been studied. Their potential response towards *p*H of aqueous solutions is quite similar with that of the *p*H glass electrode. These electrodes are in solid state and, in principle, do not involve redox reactions. Their potential is determined by the surface charge density due to the protonation and deprotonation of the PPy film surface covering the solid electrode surface. It seems that they behave as a capacitor. The deprotonated form of PPy has been used for *p*H 1.81 to 7.00, while the protonated form has been used for *p*H 7.00 to 11.92. PPy coated metallic (Au, Pt) and GC electrodes are recommended for direct and indirect *p*H determinations, as well as for electrochemical titration of neutralization.

Introduction

Conducting organic polymers represent a class of materials with electronic type conductivity. Fundamental electrochemical aspects of conducting organic polymers (including their electronic conductivity) have been detailed in many articles and reviews of the specialized literature [1÷6]. The most important polymers of this class are: polyacetylene (PAc), polypirrole (PPy), polyaniline (PAni), polythiophene (PT), poly-*p*-phenilene (PPP), polytriphenilene (PTP), polyazulene (PAz), polyfluorene (PFI), polynaphtalene (PNap), polyanthracene (PAnt), polyfuran (PFu), polycarbazole (PCz) and their derivates [2÷5].

The first successful attempt for the synthesization of these polymers was reported by Furt and co-workers [5,6] in the 1950s. However, the first electronically conducting polymeric systems with conjugated double bonds were synthesized by Dall'Olio and co-workers [7] in the late 1960s. Moreover, only in the late 1970s Heeger and co-workers [8] and Diaz and co-workers [9] discovered that these materials would undergo chemical and electrochemical redox transition to yield polymers with relatively high intrinsic electronic conductivities.

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Conducting organic polymers are a class of materials which are now competing with the classical surfaces such as metals and carbon in different electrochemical applications [10÷14]. For example, they can enhance the stability of photoelectrodes used in converting solar energy to electrical or chemical energy [4,15,16] or chemical energy to electrical energy and its stockpiling [4].

Some important aspects making modified electrodes look attractive as electrochemical tools are: the possibility of preconcentrating the analyte near or at the electrode surface, the high selective nature of the modified surface and their remarkable sensitivity. The implementation of the above properties along with some specific catalytic activity will result in minimizing high background currents by the suppression of competing redox reactions. Fouling of the electrode surface has long been a serious problem in electrochemical determinations of many organic compounds. Polymer coating of the surface of the electrode substrate helped to alleviate this problem [5,17]. On the other hand, metal and carbon electrodes with extremely small dimensions, (micro and ultamicroelectrodes) have been used for voltammetric measurements and were developed for biological, medical research and bioanalytical research, especially [18÷21].

Fleischmann and co-workers revealed in their work [22] that a decrease of the surface area of the electrode not only affects quantitative changes, but also results in unusual qualitative effects. One major advantage of microelectrodes is that the expansion of the inherently small diffusion layer on the scale time of the experiment is grater than the characteristic dimensions of the electrode. In the case of the frequently employed disk electrode such a characteristic is its radius. Relatively large diffusion layer develop a few seconds after the current starts passing through electrodes with dimensions smaller than 20 µm. The hemi-spherical diffusion (versus a planar one for conventional electrodes) leads to higher flux of the electroactive species. The mass transport coefficient m, which is a measure of the rate of transport of electroactive species in the diffusion layer, is given by the equation:

$$m = D/r\ , \tag{1}$$

where D is the diffusion coefficient and r is the electrode radius. As a result, the diffusion rate is exceptionally large as the electrode dimension decreases. Moreover, the current density at small size electrodes is relatively large (compare to conventional electrodes) and results in considerable increase in the ratio of the faradic to the capacitive currents. Thus, the property of enhanced fast mass transport was anticipated for the development of in vivo fast microvoltammetric sensors by minimizing the electrocatalytic reaction between ascorbic acid and dopamine [23]. With the help of a fast potentiostat and the use of ultramicroelectrodes it was possible to obtain fast kinetic information about the redox behaviour of conducting polymer films [24] and their electropolymerization mechanism [25]. It was also found that ultramicroelectrodes coated with polyaniline could be switched between its redox states more rapidly than has previously reported [26].

In this work, we have electrochemically deposited PPy on Pt, Au, GC stationary disc electrodes. PPy chemically modified electrodes have been tested in order to be used as potentiometric sensors for determination of the hydronium ion activity, i.e. of pH aqueous solutions. Electrochemical characteristics of the obtained modified electrodes have been determined and compared with those of the glass electrode for hydronium ions.

Experimental

All chemical used were of very high purity or reagent grade and used without further purification. Pyrrole (Fluka AG. Purum) was vacuum distilled and kept in refrigerator.

Water used for preparations of solutions and glassware washing was tridistilled. All solutions used in electrochemical measurements were deoxigenated by bubbling purified Ar stream through these solutions placed in the electrochemical cell.

Buffer solutions of *p*H 1.81 to 11.92 were prepared based on the composition of Britton-Robinson solutions.

All materials used for the preparation of the electrodes were of 99.999% purity.

Chemically modified electrodes by electrochemical covering with PPy were prepared on stationary disc Pt, Au, GC electrodes (Φ=2 mm), after they were primary polished using H_2O/alumine and washed with tridistilled water, by their immersion in an aqueous solution containing 5 ml PPy and 95 ml 0.1N HCl.

Using cycle voltammetry [16,28÷32], the potential applied to the electrode was scanned between the following limits: -0.200V and +1.400V for 5 to 10 cycles with a scan rate of 50 mV s^{-1}.

Electrochemical synthesis of PPy was carried out with a three electrodes electrochemical cell where the working electrode was the electrode to be covered by PPy, the reference electrode was SCE and the auxiliary electrode was a platinum electrode and using an M110 Radiometer recorder polarographic assembly potentiostat. For plotting voltammetric curves an LY 14010 II x – y recorder was used.

Potentiometric measurements were carried out using a two electrodes cell where the working electrode was PPy coated electrode and the reference electrode was SCE and a Cole Parmer *p*H-meter/mV-meter.

In order to compare the response of PPy modified electrodes towards the *p*H of aqueous solution, a Cole Parmer combined glass electrode has been used.

Results of discussions

Electrochemical synthesis of PPy, an electronic conductor in its oxidized form, is quickly carried out through oxidation and concomitant polymerization of PPy [32]. This process can also be readily performed by chemical oxidizing agents such as Fe(III) salts [33]. A freestanding polymer film is obtained by electrochemical way. In an oxidizing environment pyrrole typically polymerizes by linkage at its α-position, along with loss of a proton at each of these positions (Fig. 1).

The product thus prepared exists as a positively charged polymer chain that is doped with negative ions. The oxidation level is variable and the half-reaction for formation of a polymeric unit has to be written as shown in equation (2):

$$n\ PyH_2 + A^- \rightarrow (Py)_n{}^+A^- + 2n\ H^+ + (2n + 1)\ e^- \qquad (2)$$

where PyH_2 is pyrrole and A^- is dopant ion. The value of n depends on the precise conditions of the synthesis reaction and the resultant polymeric chain comprises an indefinite number of $(Py)_n^+A^-$ units.

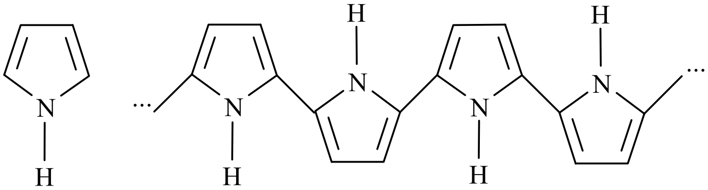


Fig. 1: *Polypyrrole (a) monomer and (b) polymer chain*

The number of PPy entities with positive charge (*n*) can be determined from the electrochemical data and the mass of polymer produced. The value of *n* thus determined usually fall between 2 and 3.

The brittle nature of ionic materials can be reduced to some degree, by the use of a long chain surfactant such as sodium dodecylbenzenesulfonate as the dopant anion in this polymer.

A PPy film can be conveniently prepared in one compartment cell using an anode and a cathode made from stainless steel. Neither the purity of the reactant nor the quality of the electronic device is critical to the success of the electrosynthesis.

In the context of the experiments discussed in this work, the PPy film was prepared in a three electrodes voltammetric cell where the working electrode on which surface the film was deposited was a stationary one with a disk form (Φ = 2 cm) and made from platinum, gold and glassy carbon, respectively. Each of these three electrodes was soaked in an aqueous solution of pyrrole and the potential was swept between –0.200 V and +1.400 V vs. SCE for 5 to 10 cycles with a scan rate of 50 cm s^{-1}, using cyclic voltammetry.

For example, Fig. 2 shows cyclic voltammograms resulted during PPy covering Au electrode. Similar voltammograms were also obtained for Pt and GC. The voltammetric curve characteristic to the first anodic sweep of the potential is responsible for the current variation at a solid electrode in the presence of pyrrole, while further successive voltammetric curves represent cyclic voltammograms of conducting PPy film because it is formed on the solid electrode and its thick is growing with successively applied potential cycling.

First voltammogram shows an anodic peak with E_{pa} = + 0.85V vs. SCE that corresponds to the pyrrole oxidation while further voltammograms exhibit a broad anodic peak with E_{pa}>1.1 V corresponding to the PPy oxidation and a cathodic peak corresponding to the PPy film reduction.

Due to its insolubility and intractability, the structure of PPy is not well characterized. The electrochemically prepared material is generally anisotropic, with layers of polymer chains parallel to the electrode surface interspersed with layers of the electrical charge balancing anions [32]. It seems that the nature of the anion may have a strong influence on the structure and the degree of anisotropy of the polymer.

Although, it has been widely studied, the mechanism of electrochemical formation of PPy has not been completely established. It has generally been accepted that the reaction is initiated by oxidation of a pyrrole molecule to form a radicalic cation. Two such species may then dimerize with the subsequent loss of two protons [34]. Dimeric or polymeric pyrrole oxidizes at a lower potential than pyrrole (Fig. 2), so propagation of the polymer may occur by the analogous addition of pyrrole radical cations to polymeric radical cations. However, other evidence suggests that these pyrrole radical cations are not involved after initiation [35] and propagation may occur by electrophilic attack of polymer radical cations on neutral monomers. There are no evidence the mechanism of chain termination but a nucleophlic attack by water to convert a PPy chain unit into a lactam ring has been proposed [36].

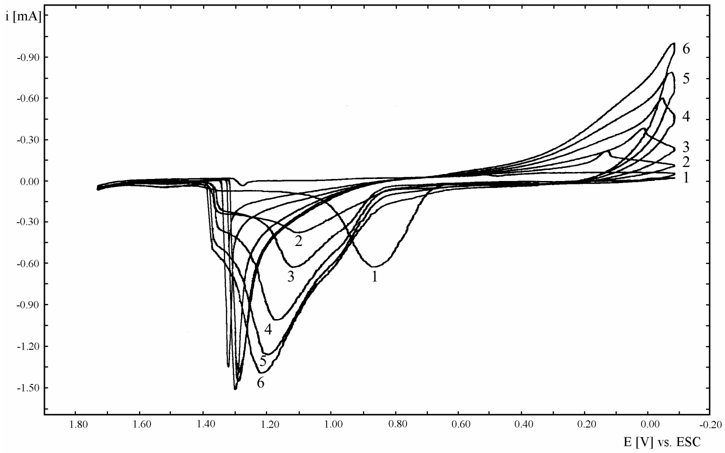


Fig. 2: *Cyclic voltammograms resulted during PPy covering Au electrode in aqueous solution of HCl 1N (95 mL) + Pyrol (5 mL) (6 cycles).*

The extent of oxidation of PPy film can be easily reflected in the value of n in equation (2) and can be altered by subjecting the film to a reducing potential. Reduction of the film requires a corresponding expulsion of dopant anions or an incorporation of cations, showing that both processes are taking place when the film is reduced [37,38]. In its reduced form PPy is a nonconductor, its conductivity increasing to a limit value with increasing of the oxidation level. However, overoxidation may cause degradation of the polymer.

Its unique proprieties have determined some new applications of the PPy, despite the lack of a full understanding of its structure and electronic conduction mechanisms. The polymer has been used in the manufacture of printed circuit boards, electrolytic capacitors, rechargeable batteries, conductive coatings for textiles [39] and chemically modified electrodes [3÷5,11,20,21] and its commercial utilization is destined to expand in the future when new knowledge of the factors that affect its mechanical and electrical proprieties is discovered.

A number of attempts for utilization of PPy electrochemically modified Pt, Au, GC solid electrodes as potentiometric sensors for direct and indirect determination of hydronium ion activity in aqueous solutions and for performing acid-base potentiometric titrations is presented in this work.

Two types of experiments have been conducted:

A. Pt, Au, GC stationary electrodes were covered by PPy through electrodepositation; then, each electrode thus prepared was used for verification of its response to variation of hydronium ion activity in Britton-Robinson buffer solutions (*p*H=1,81÷11,92), without any preliminary treatment than washing with tridistilled water for 1 min. before soaking in each buffer solutions.

B. PPy coated Pt, Au, GC electrodes have been soaked in 2 mol L^{-1} NH_4OH for 3 min., rinsed with tridistilled water and used to record the potentiometric cell voltage as a function of the *p*H of the solutions placed in the cell, from *p*H 1.81 to *p*H 7.00. Before measuring the voltage over the basic range (*p*H 7.00 to *p*H 11.92), these electrodes were soaked in a 2 mol L^{-1} HCl solution, for 3 min. and then rinsed with tridistilled water before each measurement of voltage was performed.

The Fig. 3 shows the responses of PPy coated Pt, Au, GC electrodes towards *p*H variation and the response of a hydronium ion indicator glass electrode, over a pH range between 1.81 and 11.92, for the purpose of comparison, when no other treatment has been applied to these electrodes after electrodepositation than washing with tridistilled water before each voltage measurement (the treatment A). In this conditions responses of PPy coated Pt, Au electrodes towards variation of hydronium ion activity are nearly linear with slopes of 62 mV/*p*H and 58.5 mV/*p*H, respectively, over the entire investigated range of *p*H. A slope of 54 mV/*p*H was obtained with Au electrode over a narrow range of *p*H (from 1.81 to 8.30).

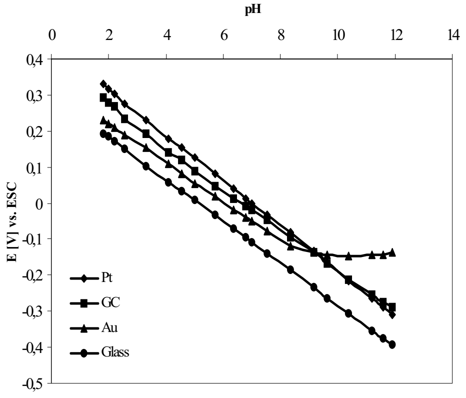


Fig. 3: *The potential variation of PPy coated Pt, Au, GC electrodes towards pH variation, without any pretreatment, comparative with response of a hydronium ion indicator glass electrode.*

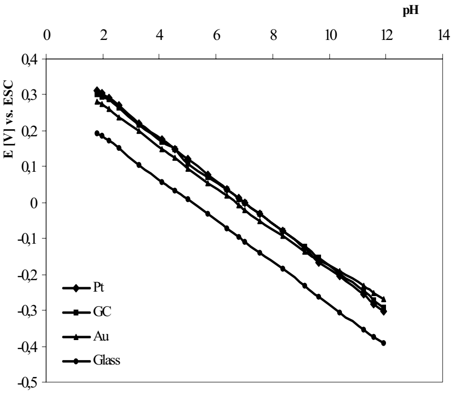


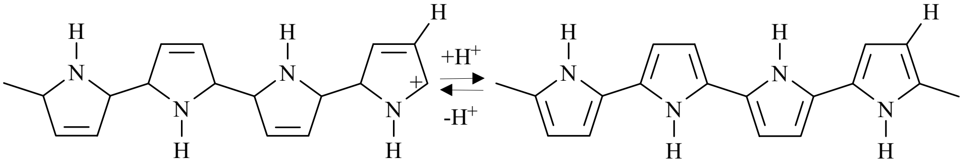
Fig. 4: *The potential variation of PPy coated Pt, Au, GC electrodes towards pH variation, with pretreatment (experiment B), comparative with response of a hydronium ion indicator glass electrode.*

Fig. 4 compares the responses of PPy coated Pt, Au and GC electrodes to the *p*H variation with that of a glass electrode (slope of 59.1 mV/*p*H) over a *p*H range from 1.81 to 11.92, when PPy coated electrodes were given treatment of soaking in a 2 mol L^{-1} NH_4OH for acid range and 2 mol L^{-1} HCl for basic range (the treatment B).

The treatment B was given to PPy coated Au, Pt, GC electrodes in order to make sure that the surface of the electrodes was in the same form before each measurement of voltage i.e. the same protonation or deprotonation form of PPy.

In this conditions, the response function of the PPy coated electrodes $E = f(p\text{H})$ is linear over the entire investigated *p*H range (1.81÷11.92) for all three type of materials with slopes of 61 mV/*p*H for Pt, 58.5 mV/*p*H for GC and 54 mV/*p*H for Au.

One reason for obtaining different values of slopes may be the different degree of protonation and deprotonation of PPy according to the equilibrium:



and also the morphology of PPy which changes depending on the surface conditions of solid surface. Thus, for obtaining reproducible and reliable results is recommended to apply the treatment B and appropriate preparation of the solid electrode surface before electrodepositation of PPy.

Conclusions

PPy chemically modified electrodes, hydronium ion indicators are nonglass electrodes with polymeric structure prepared by electrochemical way. The obtained results highlight that, in very well defined conditions, they follow the same relationship of potential and hydronium ion activity as glass electrode. The structure of electrode surface and the degree of protonation and deprotonation through the surface actives sites results in different slopes of response function.

For analytical purposes it is recommend to use PPy coated Pt and GC electrodes due to the fact that they ensure the formation of a solid PPy film, mechanical sturdiness, usability at high pressure and usability at the microscale.

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