

# The potentiometric response of polypyrrole electrosynthesised in alkaline media

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Received 8 September 2004; received in revised form 12 October 2004; accepted 14 October 2004  
Available online 16 December 2004

## Abstract

The study has been focused on the potentiometric response of polypyrrole films electrosynthesised in alkaline solutions onto vitreous carbon electrodes. The influence of different conditions for electropolymerisation and soaking on the potentiometric sensitivity of the film is analysed. A simple model allows to interpreting the ion sensitivity observed. The participation of  $\text{OH}^-$  in the ion-exchange process is demonstrated, in agreement with previous results.

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*Keywords:* Polypyrrole; Electrodeposition; Potentiometry; Ion-exchange

## 1. Introduction

It is known that the ion-exchange properties of conducting polymers results in a dependence of the open-circuit potential (OCP) on the anion and/or cation concentrations. A linear dependence of the OCP on the anion concentration logarithm was often obtained. The slope values of the potentiometric response were found to be smaller than the Nernstian response because the simultaneous cation and anion exchange [1–4]. It is accepted that the ion-exchange depends on the nature of the incorporated dopants. Thus, two extreme situations can be found: (i) when the incorporated anions are mobile in the film, anion transfer is the dominant process; (ii) when the film contains an excess of im-

mobile anions, the excess of negative charges is compensated by mobile cations.

Several theoretical models describing the OCP behaviour of conducting polymers have been presented. Doblhofer discussed the potentiometric response of polymer films in terms of Donnan equilibria prevailing at the polymer/solution interface [5]. A model which include the transport of anions, cations and electrons at the polymer/solution interface and the possible changes in the oxidation level of the polymer was analysed by Lewenstam et al. [6].

Polypyrrole (PPy) is one of the most investigated conducting polymers. Many studies have shown that the potentiometric properties of PPy films can be useful utilised in the construction of sensors [7–9].

It was found that stable conducting PPy films can be formed in alkaline solutions containing  $\text{NO}_3^-$  or  $\text{Cl}^-$  [10]. The PPy film is expected to exchange two anions,  $\text{NO}_3^-$  (or  $\text{Cl}^-$ ) and  $\text{OH}^-$ , and the cation ( $\text{Na}^+$ ) when it is cycled in a solution without the monomer. The OCP

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measurements would reflect this particular situation. There exists controversy about the participation of  $\text{OH}^-$  in the charge compensation of PPy. A decrease in the conductivity of the films with increasing pH was reported [10–13], whereas the incorporation of  $\text{OH}^-$  as a counterion has been proposed by several authors [14–18]. The contribution of  $\text{OH}^-$  is also considerable in NaOH solutions and in alkaline solutions containing anions that cannot be incorporated into the polymer film [10].

The potentiometric response should be helpful for a better understanding of the ion-exchange behaviour of the polymer matrix. Thus, the present study has been focused on the evaluation of the effects of the nature and concentration electrolyte on the potentiometric response of PPy films synthesised in alkaline solution.

## 2. Experimental

Measurements have been performed in a conventional electrochemical cell, using vitreous carbon electrodes rods ( $0.070\text{ cm}^2$ ) embedded in a Teflon holder as working electrodes, a platinum counterelectrode and a saturated calomel electrode. Polymerisation and potentiometric measurements have been performed using a linear voltage sweep generator PAR model 175, a potentiostat-galvanostat PAR model 173 and HP 4007 B  $x-y$  recorder.

The surface of the working electrode was polished prior to polymerisation with sand paper to achieve good adhesion of the polymer film. Deposition of Ppy films was carried out potentiostatically at  $E = 0.90\text{ V}$  for 90 s from solutions containing  $0.5\text{ M Py}$  in a purified gas saturated atmosphere at  $25^\circ\text{C}$ . The electrodeposition charge was usually  $1\text{ C}$ . The as-prepared Ppy-covered electrodes were immersed for 5 h in  $10^{-1}\text{ M}$  solution of the salt to be tested. Then, the electrode potential was recorded in the electrolyte solution saturated with nitrogen until a constant value was obtained ( $\pm 1\text{ mV}$ ).

Solutions of different salts as  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , NaDBS (sodium dodecylbenzene sulfonate),  $\text{Na}_2\text{C}_2\text{O}_4$  (sodium oxalate) and  $\text{NaCH}_3\text{CO}_2$  (sodium acetate) were used. All chemicals were reagent grade and solutions were freshly made in twice distilled water. The pH of the solutions was adjusted by addition of NaOH. Py was purchased from Acros Organics and it was freshly distilled under reduced pressure before use.

## 3. Results and discussion

The potentiometric response in NaOH solutions with pH values between 10.5 and 13 of PPy film prepared in  $0.1\text{ M NO}_3^-$ , pH 12 solution containing Py, is shown in Fig. 1. The slope value of the linear plot satisfies a

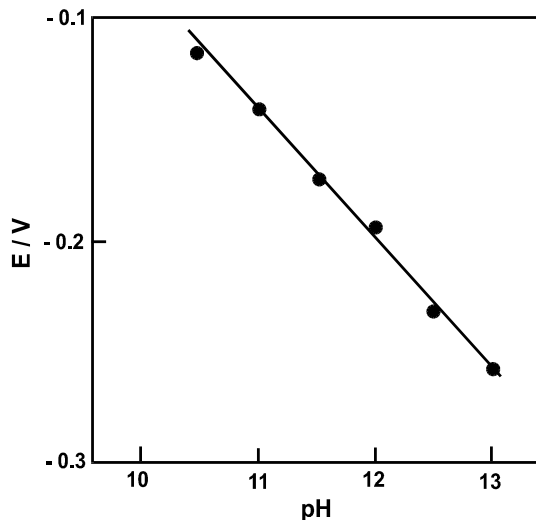


Fig. 1. Dependence of the open-circuit potential recorded for PPy film on pH of NaOH solutions. The film was formed potentiostatically in  $0.1\text{ M NO}_3^-$ , pH 12 solution containing  $0.5\text{ M Py}$ .

Nernst response. The anionic sensitivity observed is obviously determined by  $\text{OH}^-$ , the only anion present in the solution. The same response was obtained for solutions of the same pH but containing  $0.1\text{ M C}_2\text{O}_4^{2-}$  or  $0.1\text{ M CH}_3\text{CO}_2^-$ . Under the present experimental conditions there is no evidence for overoxidation of the polymer film.

Fig. 2 shows the OCP-log (nitrate concentration) response for a PPy formed in alkaline solution and then immersed in an alkaline solution containing different  $\text{NO}_3^-$ -concentrations. The OCP of the PPy film is almost independent on  $\text{NO}_3^-$  concentrations for the lower con-

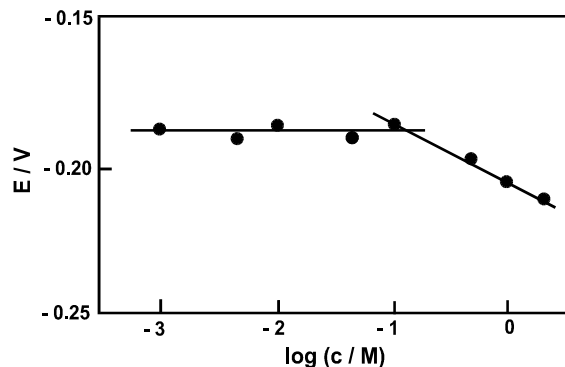
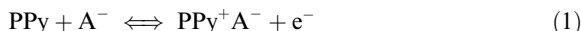


Fig. 2. Dependence of the open-circuit potential recorded for PPy film on logarithm of  $\text{NaNO}_3$  concentration (pH 12). The film was formed potentiostatically in  $0.1\text{ M NO}_3^-$ , pH 12 solution containing  $0.5\text{ M Py}$ .

centrations used in this study, whereas an anionic response is obtained at higher concentrations.

The electrochemical redox process of PPy may be expressed as



where  $\text{A}^-$  is the anion and PPy and  $\text{PPy}^+$  represents the reduced and oxidised polymer.

Data can be analysed by the simplest way, that is the use of the Nernst equation, assuming the oxidation level of the polymer remains constant. The potential of the modified electrode may be expressed by the equation:

$$E = E^0 - (RT/F) \ln[\text{A}^-] \quad (2)$$

where  $E^0$  is a constant and  $[\text{A}^-]$  is the anion concentration in solution.

The redox reaction in the presence of two mobile anions can be expressed as



In this case, the potential may be expressed by the equation:

$$E = E^0 - (RT/F) \ln([\text{A}_1^-]^x [\text{A}_2^-]^y) \quad (4)$$

If  $x$  and  $y$  are determined by the transport number ( $\tau$ ) of each ion [4], the Eq. (4) can be rewritten as

$$E = E^0 - \tau_{\text{A}_1^-} (RT/F) \ln[\text{A}_1^-] - \tau_{\text{A}_2^-} (RT/F) \ln[\text{A}_2^-] \quad (5)$$

If anions are partially blocked, the electroneutrality of the polymer is also reached by cation ( $\text{C}^+$ ) insertion, and the OCP dependence of the polymer of both cation and anions concentration in solution can be described by the following equation:

$$E = E^0 - \tau_{\text{A}_1^-} (RT/F) \ln[\text{A}_1^-] - \tau_{\text{A}_2^-} (RT/F) \ln[\text{A}_2^-] + \tau_{\text{C}^+} (RT/F) \ln[\text{C}^+] \quad (6)$$

The Nernst response obtained in Fig. 1 confirms that  $\text{OH}^-$  acts in the role of charge compensation of the polymer. This result also indicates that cations are not involved in the compensation of this charge. When the PPy film is synthesised in acid solution (0.1M  $\text{HNO}_3$  + 0.5M Py) the linear correlation shown in Fig. 1 is missing. It was shown that PPy films formed in acid solutions are less stable to cycle in alkaline media than those films formed in alkaline solutions [10]. The present results may be related with this fact.

On the other hand, the OCP is practically independent of salt concentration when the alkaline solution contains the lower concentrations of  $\text{NO}_3^-$  (Fig. 2). This is probably due to the ion-exchange equilibrium is determined mainly by the  $\text{OH}^-$ . As the  $\text{NO}_3^-$  concentration increases, a linear dependence is observed, but the magnitude of the slope ( $0.020 \text{ V dec}^{-1}$ ) indicates that  $\text{NO}_3^-$  is not the only species involved in the exchange process. From the data it is impossible to determine whether

$\text{OH}^-$  or  $\text{Na}^+$  is the other species involved. It is reasonable to suppose that in this case the transport of the cation does not take place or that its contribution is not important, as occurred in NaOH solution. Thus,  $\text{NO}_3^-$  and  $\text{OH}^-$  participates in the ion-exchange equilibrium, following the dependence given in Eq. (5). Considering the slope value and anion concentrations, it can be inferred that the contribution of  $\text{OH}^-$  to the ion-exchange process is considerable. The diffusion coefficient of  $\text{NO}_3^-$  into PPy/nitrate films was considered similar to that of  $\text{OH}^-$  in  $\text{Ca}(\text{NO}_3)_2$  solutions [18].

It has been shown that the dependence between OCP and solution pH of PPy formed in alkaline media exhibits a linear relationship with a slope deviated from the Nernst value in the potential range between 6 and 13 [10]. This result was interpreted considering the simultaneous exchange of  $\text{OH}^-$  and  $\text{NO}_3^-$ . At lower pH values a deviation from the linearity was observed.

The OCP was also measured in neutral solutions. Prepared PPy films in alkaline solution were transferred into  $\text{NO}_3^-$ -solutions at pH 7. The polymer gives an anionic response with a small slope of  $0.018 \text{ V dec}^{-1}$  (Fig. 3,

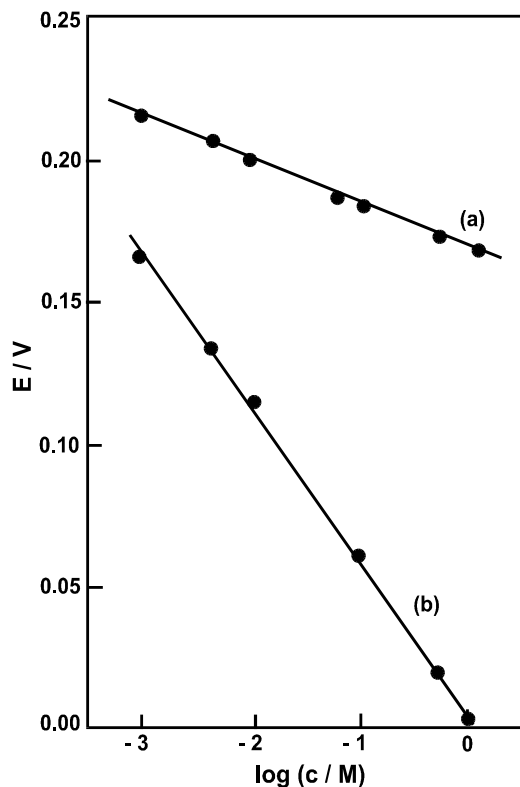


Fig. 3. Dependence of the open-circuit potential recorded for PPy film on logarithm of  $\text{NaNO}_3$  concentration (pH 7). The film was formed potentiostatically in (a) 0.1M  $\text{NO}_3^-$ , pH 12 solution containing 0.5M Py; (b) 0.1M  $\text{HNO}_3$  solution containing 0.5M Py.

curve a). For comparison, an analogous experiment was performed for PPy films formed in acid media. The dependency obtained is different in this case. The slope values of the linear plot satisfy a Nernst response to  $\text{NO}_3^-$  (Fig. 3, curve b), in accordance with the results reported by Pei and Qian [2]. The Nernst response obtained for films formed in acid media indicates that the ion exchange equilibrium between polymer and solution is determined by  $\text{NO}_3^-$ . The contribution of  $\text{NO}_3^-$  to the ion-exchange diminishes when the film is formed in alkaline media (Fig. 3, curve a). Previous results showed there is a  $\text{Na}^+$  ingress from the solution when the film formed in alkaline media is potentiodynamic polarised in a neutral solution [10]. Thus, the deviation from the Nernst value is probably due to the simultaneous participation of the cation, as predicted by Eq. (6) with  $\tau_{\text{A}_2^-} = 0$ . Considering the negative slope, it can be inferred that the transfer of  $\text{NO}_3^-$  is dominant ( $\tau_{\text{NO}_3^-} > \tau_{\text{Na}^+}$ ).

The potentiometric response of PPy film formed in alkaline solutions containing sulphate was also tested (Fig. 4). A linear relationship between the electrode potential and  $\log$  (sulphate concentration) with a negative slope ( $-0.030 \text{ V dec}^{-1}$ ) is obtained for sulphate concentrations in the range 0.001–0.1 M. Increasing the sulphate concentration the slope is reversed. The polymer gives a cationic response as can be seen in Fig. 4. The negative slope of the OCP vs  $\log$  (sulphate concentration) dependence for the lower electrolyte concentrations and the cationic response in the more concentrated solutions can be explained considering the low mobility of sulphate into the polymer film [4]. It is reasonable to suppose that if anionic sensitivity was due to sulphate, this response should not change at higher concentrations. Thus, the ion-exchange equilibrium is determined principally by  $\text{OH}^-$  for low sulphate concentrations and

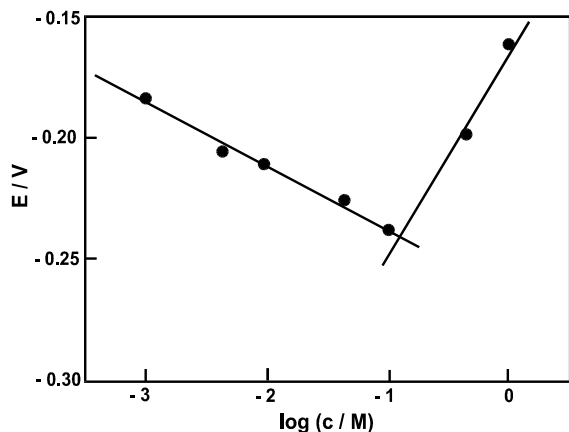


Fig. 4. Dependence of the open-circuit potential recorded for PPy film on logarithm of  $\text{Na}_2\text{SO}_4$  concentration (pH 12). The film was made potentiostatically in 0.1 M  $\text{SO}_4^{2-}$ , pH 12 solution containing 0.5 M Py.

by  $\text{Na}^+$  for the higher ones. The cationic sensitivity is consistent with that reported by Tamm et al. [4]. The authors explained the cationic sensitivity considering that diffusion of the dopant anion in the polymer is

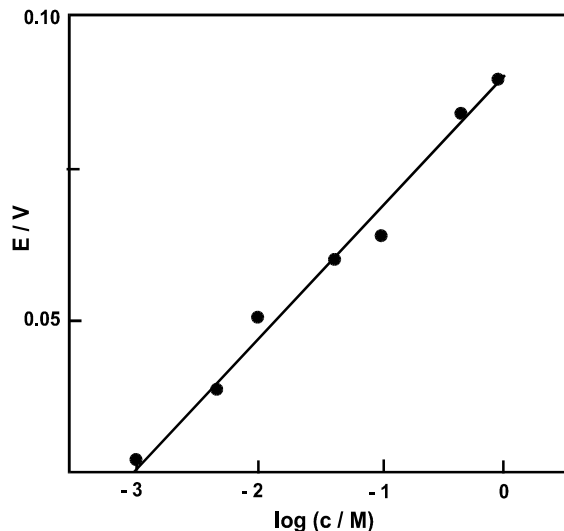


Fig. 5. Dependence of the open-circuit potential recorded for PPy film on logarithm of  $\text{Na}_2\text{SO}_4$  concentration (pH 7). The film was made potentiostatically in 0.1 M  $\text{SO}_4^{2-}$ , pH 12 solution containing 0.5 M Py.

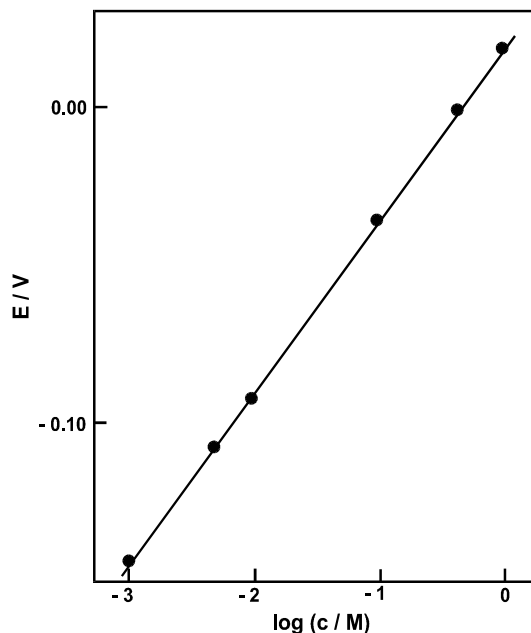


Fig. 6. Dependence of the open-circuit potential recorded for PPy film on logarithm of  $\text{NaNO}_3$  concentration (pH 7). The film was formed potentiostatically in 0.1 M  $\text{DBS}^-$ , pH 12 solution containing 0.5 M Py.

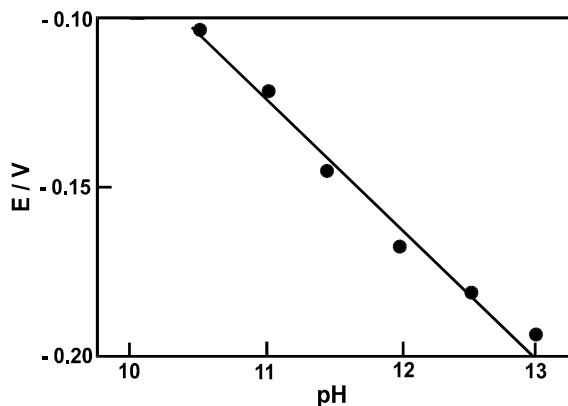


Fig. 7. Dependence of the open-circuit potential recorded for PPy film on pH of NaOH solutions. The film was formed potentiostatically in 0.1M DBS<sup>-</sup>, pH 12 solution containing 0.5M Py.

low and ion-exchange equilibrium between the polymer and solution is carried out mainly by cation. The participation of the cation occurs for all the range of concentrations when the response is analysed in neutral solutions (Fig. 5).

The dependence of the potential on the nitrate concentration in neutral solution is different when the PPy film was formed in alkaline solutions containing a surfactant (DBS<sup>-</sup>). A linear dependence with a positive slope is recorded, indicating that cations are mainly involved in the ion-exchange process (Fig. 6). Fig. 7 shows the dependence of the potential on NaOH concentration. A negative slope of the OCP vs pH ( $-0.038 \text{ V dec}^{-1}$ ) was obtained, in contrast with the Nernstian value obtained when the film is formed in NO<sub>3</sub><sup>-</sup> solution (Fig. 1). The anionic response indicates that OH<sup>-</sup> participates in the ion-exchange equilibrium. The fact that a sub-Nernstian value was obtained seems to be associated with the simultaneous transport of OH<sup>-</sup> and Na<sup>+</sup> in the polymer matrix.

#### 4. Conclusions

Measurements of the dependence of the electrode potentials of Ppy-coated vitreous carbon electrodes formed in alkaline solutions on the electrolyte concentrations support the following propositions:

- The incorporation of OH<sup>-</sup> as a counter ion when the film is immersed in NaOH solutions.
- The participation of OH<sup>-</sup> and NO<sub>3</sub><sup>-</sup> in the ion-exchange equilibrium in alkaline solutions containing nitrate.
- The participation of OH<sup>-</sup> and Na<sup>+</sup> in the ion-exchange equilibrium in alkaline solutions containing sulphate or sodium dodecylbenzene sulfonate.

#### Acknowledgments

Fundación Antorchas, Consejo Nacional de Investigaciones Científicas y Técnicas and Universidad Nacional del Sur, Bahía Blanca, Argentina are acknowledged for financial support.

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