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Polymer 46 (2005) 12233–12239

polymer

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# Potentiometric pH sensors based on electrodeposited polymers

Boris Lakard *, Guillaume Herlem, Sophie Lakard, René Guyetant, Bernard Fahys

*LCMI, Université de Franche-Comté, 16 route de Gray, 25030 Besançon cédex, France*

Received 20 January 2005; received in revised form 18 October 2005; accepted 20 October 2005
Available online 8 November 2005

## Abstract

Five potentiometric pH sensors based on thin polymer films, obtained from electropolymerization of their respective monomers: 1,3-diaminopropane, diethylenetriamine, pyrrole, *p*-phenylenediamine and aniline, were compared. All these molecules have been chosen since they contain amino groups, which are sensitive to proton concentration changes. The resulting sensors consist in a polymer-coated smooth platinum wire protruded from glass sheath. Their potentiometric responses appeared linear in the range from pH 2 to 11. These electrodes present also a good reversibility and a good stability in time over a period of 1 month. The response mechanisms are also examined.

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*Keywords:* Electrochemical polymerization; Surface modification; Potentiometric pH sensors

## 1. Introduction

pH measurements are performed a countless number of time every day, in all pH dependant chemical processes, especially in crucial areas such as agribusiness, pharmaceutical industry and human health. Despite the importance to monitor accurately the pH changes in aqueous media, there are not many ways to control the acidity (or basicity). Currently, the most frequently used electrode for measuring pH remains traditional glass membrane pH electrodes, which have the disadvantage to be delicate and expensive. The main alternative to these electrodes is a structure containing a metal oxide, which acts as the active component. pH response has been observed for certain types of electrically semi-conducting oxides, in particular lead, cobalt, iridium or molybdenum oxides [1–4]. These metallic oxide-based electrodes can be miniaturized but they have the disadvantage to be toxic. Consequently, there is a need for new pH sensors. For example polymer-based pH electrodes, which are biocompatible and cheap, can be miniaturized to be used in clinical or biological applications, such as in vivo analysis. Historically, the first pH sensor resulting from the electropolymerization of chemical compounds at electrode surfaces was elaborated by Heineman in 1980 [5]. Indeed, he electrodeposited a film of poly(1,2-diaminobenzene) on a platinum electrode and he found a near Nernstian potentiometric response to pH changes. Since these first experiments, there has been a growing interest in electropolymerized film chemically modified electrodes and their application as potentiometric pH sensors since the protonation of nitrogen or oxygen atoms in the polymers are expected to impart a pH response to the chemically modified electrodes.

Thus, electrosynthesized polymers are considered to be good candidates as pH sensors due to the fact that they are strongly bonded to the electrode surfaces during the electropolymerization step. In addition, thanks to the presence of amino groups, for example onto the modified surfaces, it is possible to imagine that chemically modified electrodes will exhibit potentiometric responses depending on the pH changes. This is the reason why we have tested these polymer coatings as pH sensors in aqueous solutions. In a first time, we have tested pH sensors using electropolymerized polyethyleneimine (PEI), and polypropyleneimine (PPI), modified platinum electrodes since we have found a new way to synthesize them allowing us to coat electrodes with a film of PEI or PPI [6]. The potentiometric responses to pH changes appeared linear, reversible and stable in time thanks to the amino groups present in the polymer backbone [7,8]. We also want to test other electrosynthesized polymers containing amino groups to compare their potentiometric responses with those of PEI and PPI. In this aim, we have tested electrosynthesized polypyrrole,

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* Corresponding author. Tel.: +33 3 81 66 62 98.
*E-mail address:* boris.lakard@univ-fcomte.fr (B. Lakard).

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doi:10.1016/j.polymer.2005.10.095

poly(*p*-phenylenediamine) and polyaniline modified platinum electrodes.

## 2. Experimental

### 2.1. Reagents

All the electrolytes: 1,3-diaminopropane (1,3-DAP), diethylenetriamine (DETA), pyrrole (Py), aniline (Ani) and *p*-phenylenediamine (PPD) were obtained from Sigma–Aldrich (analytical grade) and used as received. *N*-Lithiofluoromethanesulfonimide (LiTFSI) is obtained from Sigma–Aldrich and used as a supporting electrolyte at a concentration of $10^{-2}$ M, and was added to 1,3-DAP and DETA in a glove box (Jacomex, France) under electronic grade Ar stream (Air Liquide, France) equipped with $H_2O$ and $O_2$ traps. Solutions of HCl (0.8 M) and KCl 0.1 M in a phosphate buffer solution of pH = 7.0 (Titrinorm grade according National Institute of Standards and Technology), from Prolabo (France) were prepared and stored at +4 °C. Py was used at the concentration of 0.1 M in a the solution of KCl, PPD at the concentration of 0.1 M in the phosphate buffer solution and Ani at the concentration of 0.2 M in the 0.8 M solution of HCl previously prepared.

### 2.2. Apparatus

All cyclic voltammetry experiments were carried out and recorded with an Autolab potentiostat galvanostat, model PGSTAT 20 (Ecochemie, The Netherlands), controlled by a PC computer via GPES 4.2 software interface. The electrochemical cell consisted in a classical three-electrode set-up with an Ag wire as the reference electrode (noted SRE for silver reference electrode), a platinum disk as the counter-electrode and a smooth platinum disk electrode (0.785 $mm^2$ area) as the working electrode. Electrode potential in the different buffered solutions were measured versus a saturated calomel electrode (SCE), XR100 model from Radiometer Analytical-France, via a pH meter, PHN130T model (Tacussel electronics-France), used as a high impedance voltmeter ($>10$ MΩ). Each potentiometric measurement was performed at about ±1 mV.

Synthesized polymers were characterized using a NEXUS 470 spectrophotometer coupled to an Omnic software from Nicolet to perform IR–ATR spectra.

Examinations of polymer topography and morphology were performed using a high-resolution scanning electron microscope (SEM). Once synthesized and dried, polymer samples prepared for high-resolution SEM were sputter-coated with a thin (thickness: 5–10 nm) conductive layer of gold in an argon atmosphere at 0.05 mbar (Cressington 108, Watford, UK). Then, samples were examined in a scanning electron microscope LEO (SEM LEO stereoscan 440, manufactured by Zeiss–Leica, Köln, Germany) with an electron beam energy of 15 keV.

## 3. Results

### 3.1. Electrodeposition and characterization of polymer films on platinum electrodes

#### 3.1.1. Electrodeposition of polymer films on platinum electrodes

*3.1.1.1. Electrodeposition of polypyrrole.* Polypyrrole (PPy) films were electrodeposited onto smooth platinum electrodes, consisted in a platinum wire protruded from glass sheath, by means of cyclic voltammetry method in solutions composed of $10^{-1}$ M pyrrole and $10^{-1}$ M KCl in a phosphate buffer solution (pH = 7.0). In order to prepare the electrodes, two scans between 0 and +4 V/SRE were performed at 40 mV/s (Fig. 1(a)). We observed the oxidation peak at a potential of +2.4 V/SRE during the first scan which is characteristic from the oxidation of −NH groups. More, this polymer is a conductive one since this oxidation peak can be observed for the second scan with a similar current at the peak potential.

*3.1.1.2. Electrodeposition of polyparaphenylenediamine.* Poly(*p*-phenylenediamine) (PPPD) was electrosynthesized by anodic oxidation of a solution of PPD, swept in pH = 7.0 phosphate buffer, from −2 to +4 V/SRE at 20 mV/s at a platinum electrode (Fig. 1(b)). It can easily be noticed that the electrochemical oxidation of PPD was completely irreversible and the oxidation peak can be observed at a potential of +1.6 V/SRE. The oxidation current of PPD is constant during successive steps. This behavior is indicative of the formation of a conductive polymer film on the electrode surface.

*3.1.1.3. Electrodeposition of polyaniline.* Polyaniline (PANI) is a well-known conductive polymer that we have electrodeposited onto smooth platinum electrodes by oxidation of a solution composed of 0.2 M aniline and 0.8 M HCl. In order to passivate the electrode, two scans between 0 and +1.5 V/SRE were performed at 20 mV/s (Fig. 1(c)). We can observe an oxidation peak at the potential of +0.95 V/SRE during the first scan. This peak corresponds to the of amino group oxidation.

*3.1.1.4. Electrodeposition of polyalkyleneimines.* Polyethyleneimine (PEI) and Polypropylèneimine (PPI) films were electrosynthesized from solutions composed of 10–2 M LiTFSI in pure solvent (the solvent was DETA or 1,3-DAP). The electrodes were passivating in a 10–2 M LiTFSI solution of pure DETA or 1,3-DAP. During the first scan we increase the potential from 0 to +3 V/SRE, then the potential of +3 V/SRE is maintained during 60 min. Then we decrease the potential from 3 to +0 V/SRE. Finally we are doing an additional scan between 0 and +3 V/SRE. (Fig. 1(d) and (e)). While the polymer film growth at the electrode surface, there is a drastic decrease of the current value that can be linked to the electrical insulating property of these polymers. Following

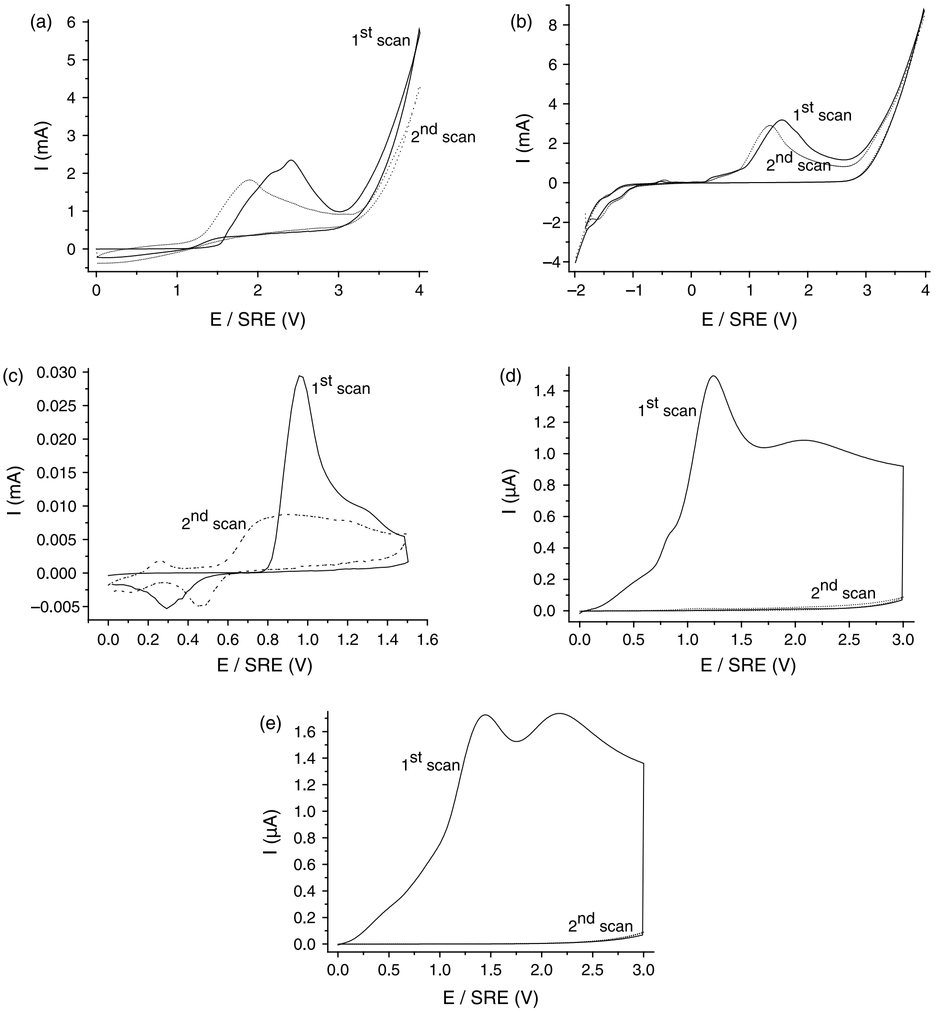

Fig. 1. Cyclic voltammograms of: $10^{-1}$ M Py + $10^{-1}$ M KCl in a phosphate buffer solution, (a); $10^{-1}$ M PPD in a phosphate buffer solution with an electrode biased during 1 min at +4 V/SRE, (b); 0.2 M Ani +0.8 M HCl, (c); $10^{-2}$ M LiTFSI in pure DETA, (d); and $10^{-2}$ M LiTFSI in pure 1,3-DAP, (e).

scan allows us to check the stability and the insulating property of the coating.

Once these electropolymerization processes finished, all the chemically modified platinum electrodes were rinsed with water and absolute ethanol, dried in an oven (at 40 °C), and tested in several buffered solutions of different pH values.

### *3.1.2. Characterization of the polymeric films*

In order to check the chemical nature of the synthesized polymeric films, we performed IR–ATR spectra from all the electrodeposited films. These spectra allow us to identify the electrodeposited films. Thus, the vibrational bands observed in the IR–ATR spectra of oxidized Ani, PPD, Py, DETA and 1,3-DAP are compiled in Table 1. As expected, these bands are

Table 1
Vibrational bands of oxidized monomers

| Vibration band | Oxidized Py ($cm^{-1}$) | Oxidized PPD ($cm^{-1}$) | Oxidized Ani ($cm^{-1}$) | Oxidized DETA ($cm^{-1}$) | Oxidized DAP ($cm^{-1}$) |
|---|---|---|---|---|---|
| N–H stretching secondary amine | 3332 | 3200 | 3250 | 3300–3200 | 3300 |
| N–H deformation | 1698 | 1678 | 1620 | 1600 | 1570 |
| C–N stretching | 1350 and 1280 (aromatic) | 1283 and 1251 (aromatic) | 1290 and 1255 (aromatic) | 1100 | 1125 |
| C–H stretching | 3030 (aromatic) | 3040 (aromatic) | 3050 (aromatic) | 2930 and 2860 | 2930 and 2880 |
| C–H deformation | 700 and 800 (aromatic) | 827 (aromatic) | 750 (aromatic) | 1500 | 1490 and 1500 |
| C–C aromatic stretching | 1560 and 1447 | 1499 and 1450 | 1595 and 1495 | – | – |
| Polymer synthesized | PPy | PPPD | PANI | PEI | PPI |

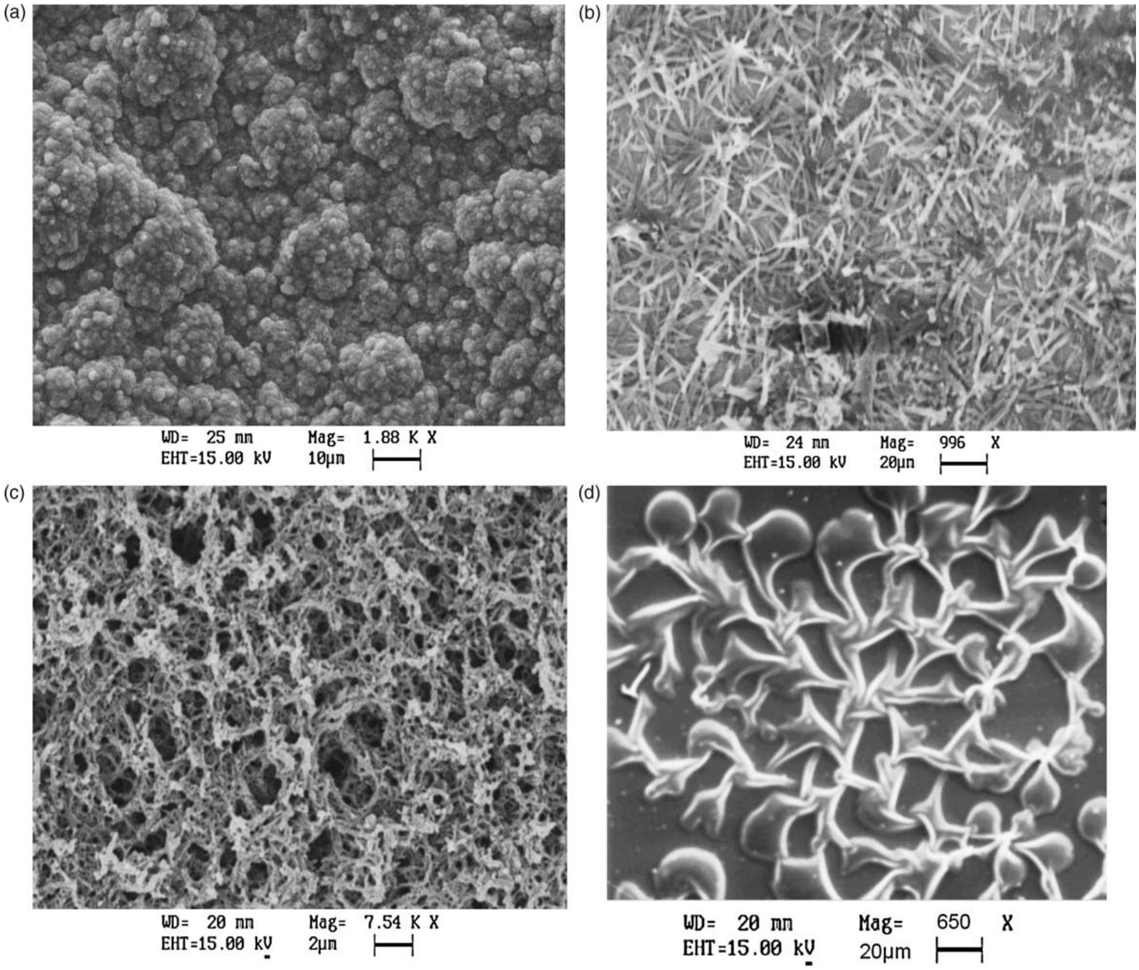

Fig. 2. SEM images of platinum electrodes (area: 0.785 mm$^2$): (a) PPy-modified, (b) PPPD-modified, (c) PANI-modified, (d) PEI-modified, respectively. The electron beam energy was 15 keV for all the images.

characteristic from PANI, PPPD, PPy, PEI and PPI, respectively.

### 3.2. Scanning electron microscopy

SEM studies were carried out on passivated platinum electrode surfaces. Resulting images of an electrosynthesized PPy film shows a compact, globular structure with the formation of aggregates (Fig. 2(a)). The aggregates size is ranging from 5 to 20 µm. Fig. 2(b) shows that the growth of PPPD film on platinum electrodes is a dentritic one. More, the polymer surface appears porous and reveals a coral-like needle structure. Fig. 2(c) shows that the PANI growth from acidic media resulted in a sponge-like, branched, porous-structured, high surface area polymer film on platinum. This structure is ideal for inclusion of molecules, especially protons. Polyalkyleneimine coatings exhibit a clover-like structure and the surface is homogeneously covered by the PEI and PPI coatings (Fig. 2(d)). These SEM images will be used to explain the potentiometric responses to pH values (Section 3.3).

### 3.3. Use of chemically modified electrodes as potentiometric pH sensors

#### 3.3.1. Potentiometric responses to pH changes of chemically modified electrodes

*3.3.1.1. Response time and reversibility.* We have examined the potentiometric responses of the modified platinum electrodes as a function of the changes in pH. In all cases the electrodes were immersed into different buffered solutions. The potential equilibrium response time varies from one polymer-coated electrodes to the other. Indeed, the response time are faster for PEI and PPI (approximately 15 s) than for PANI (1 min), PPPD (1 min) and PPy (2 min).

The potentiometric response reversibility of chemically modified electrodes was also tested by comparing their potentiometric responses when the measurements are performed for increasing and decreasing pH. It appeared that the potentiometric responses did not show significant dependence on the direction of pH changes since the differences between potentiometric responses obtained with increasing and decreasing measurements are inferior or equal to 5 mV.

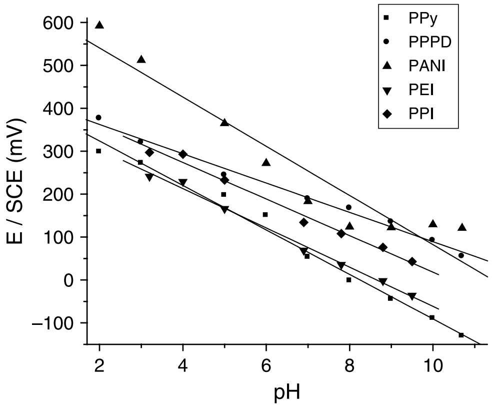

Fig. 3. Potentiometric responses to pH changes of the platinum electrodes chemically modified by electropolymerization.

Table 2
Evolution of the potentiometric responses $E$ for the different chemically modified

| Polymer modified-electrode | Slope of $E$ (mV) = $f$ (pH) (in mV/pH unit) | Correlation coefficient |
|---|---|---|
| PPy | −48 | 0.9966 |
| PPPD | −34 | 0.9950 |
| PANI | −52 | 0.9573 |
| PEI | −46 | 0.9967 |
| PPI | −43 | 0.9937 |

So we can consider that the potentiometric responses did not show dependence on the direction of pH changes. More we noticed experimentally that roughly the same potentiometric responses are obtained when the pH values vary in some random manner.

*3.3.1.2. Potentiometric responses.* The potentiometric responses, at different pH values, of the modified electrodes were gathered Fig. 3. We used these measurements to modelize the behavior of these electrodes by calculating the linear regression of the potentiometric responses as a function of the pH values. The linear regression correlation coefficients are superior to 0.99 for all polymers except PANI (Table 2). Consequently, we can assume that nearly all the chemically modified electrodes showed a linear behavior from pH = 2–11. More, the slopes of these linear regressions help us to compare the response sensitivity of each modified electrodes. Thus, it appears that PPPD-modified electrodes give the less important potential responses to pH changes since the slope obtained is −34 mV/pH unit. Excepted for PPPD-modified electrodes, potential responses are in the range from −43 mV/pH (PPy) to −48 and −52 mV/pH for the most important ones (PPy and PANI, respectively). We can also remember that PPy and PANI have a compact and homogeneous structures as it was shown using scanning electron microscopy (Section 3.2). Consequently, we can assume that the homogeneity of their structures enables these coating to give more important potential responses to pH changes. On the contrary, PPPD has an unhomogeneous structure and exhibits a less important potential response to pH changes.

### *3.3.2. Influence of the ageing on the potentiometric responses of chemically modified electrodes*

The potentiometric responses of the chemically modified electrodes were examined over a period of 30 days in order to test their stability in time (Table 3).

We observed that chemically modified electrodes show a linear behavior from pH = 2.0–11.0 during 30 days as illustrated by the correlation coefficients $R$ which remain nearly constant during the period of test since $R > 0.99$ for all polymers after 30 days of test.

For PPPD (Fig. 4(a)), PPI (Fig. 4(b)): the potentiometric responses are stable in time since the sensitivity remains roughly constant over all the period of test and since the correlation coefficient remain roughly constant too. For example, in the case of PPPD-modified electrode, all the slope values vary between 29 and 34 mV/pH unit and the correlation coefficient between 0.9929 and 0.9995.

Table 3
Evolution of the potentiometric responses $E$ as a function of pH changes for the different chemically modified electrodes during 30 days

| Monomer | 1st day | 2nd day | 5th day | 10th day | 15th day | 20th day | 25th day | 30th day |
|---|---|---|---|---|---|---|---|---|
| PPy | | | | | | | | |
| $s$ | −48 | −51 | −49 | −42 | −42 | −40 | −38 | −33 |
| $R$ | 0.9963 | 0.9981 | 0.9925 | 0.9851 | 0.9875 | 0.99076 | 0.9924 | 0.9923 |
| PPPD | | | | | | | | |
| $s$ | −34 | −33 | −29 | −33 | −35 | −30 | −31 | −30 |
| $R$ | 0.9950 | 0.9929 | 0.9944 | 0.9961 | 0.99795 | 0.9986 | 0.9995 | 0.9946 |
| PANI | | | | | | | | |
| $s$ | −52 | −45 | −44 | −47 | −44 | −45 | −43 | −44 |
| $R$ | 0.9573 | 0.9752 | 0.9826 | 0.9945 | 0.9902 | 0.9962 | 0.9952 | 0.9938 |
| PEI | | | | | | | | |
| $s$ | −46 | −45 | −42 | −40 | −39 | −33 | −34 | −44 |
| $R$ | 0.9967 | 0.9967 | 0.9983 | 0.9995 | 0.9988 | 0.9969 | 0.9991 | 0.9932 |
| PPI | | | | | | | | |
| $s$ | −43 | −43 | −45 | −41 | −38 | −39 | −38 | −40 |
| $R$ | 0.9937 | 0.9950 | 0.9962 | 0.9981 | 0.9959 | 0.9959 | 0.9950 | 0.9982 |

$s$, slope in mV/pH unit; $R$, correlation coefficient.

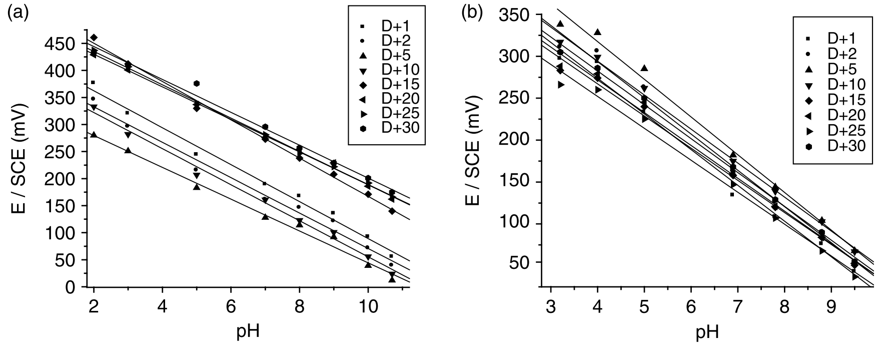

Fig. 4. Potentiometric responses to pH changes of the platinum electrodes chemically modified by electropolymerization of PPPD, (a); and PPI, (b).

If we are looking in more details the results obtained for each polymer, we can observe that:

- potentiometric responses to pH changes of PPy and PEI films remain linear during all the period of test as shown by the correlation coefficient but the sensitivities of these coatings decrease considerably with time since the slope varies from 48 (1st day) to 33 mV/pH unit (the 30th day) for PPy and from 46 (1st day) to 34 mV/pH unit (the 30th day) for PPy. Consequently PEI and PPy coatings are not stable over a period of 1 month and the sensors cannot be used for several measurements. However, PPy and PEI can be interessant for one-use sensor thanks to its sensitivity during the first measurements,
- sensitivity of PANI films is more important than the sensitivity of other polymers tested. However, the correlation coefficient is not good enough to be sure that the potentiometric responses to pH values of PANI is linear in the range going from pH = 2.0 – 11.0. In fact, it seems that this response is always linear from pH = 2.0 – 9.0 but not for pH superior to pH = 9.0. Consequently, the PANI coating sensitivity makes PANI a good candidate for applications concerning pH measurements below to pH 9.0,
- sensitivity of PPPD films is less important than the sensitivity of other polymers tested. However, the PPPD film potentiometric responses are stable in time since the correlation coefficient remains superior to 0.99 during the whole period of test and since the sensitivity remains constant too. Consequently PPPD coatings can be use for multi-use sensors,
- PPI coatings are nearly as stable as PPPD films as indicated by the correlation coefficient and slopes of Table 3. However, the sensitivity of PPI films is better than the sensitivity of PPPD films. Consequently, these PPI coatings can also be used for multi-use sensors and they seem to be the most promising polymer coating between the different ones tested. Moreover, since PPI films are biocompatible, they can also be used for local pH measurements in biomedical applications and in vivo analysis.

### *3.4. Response mechanism*

We have shown that the potentiometric responses to pH changes of the different biased electrodes are linear in the range 2–11. These responses must be mainly attributed to the polymer films rather than the platinum substrate [7,8]. A possible explanation is the affinity of the numerous amino groups to the protons in solutions. The reaction of $H^+$ onto amino groups creates local charge density excess at the electrode surface. Surface reactions seem to take place on the polymer film, essentially protonation and deprotonation of superficial amino groups of the polymers as symbolically described by the Eq. (1):

$$\mathrm{P(Polymer)} + \mathrm{H}^+ \rightarrow \mathrm{PH}^+ \tag{1}$$

When the equilibrium is reached at the polymer/solution interface, we can write the equilibrium expression K of the surface reaction (1) and the equilibrium potential $E$ as:

$$\mathrm{K} = \frac{[\mathrm{PH}^+]}{([\mathrm{P}][\mathrm{H}^+])} \tag{2}$$

and

$$E = E_0 + \left(\frac{RT}{F}\right)\ln\left(\frac{[\mathrm{PH}^+]}{[\mathrm{P}]}\right) = E_0' + \left(\frac{RT}{F}\right)\ln[\mathrm{H}^+] \tag{3}$$

According to this mechanism of reaction, we are waiting for a potentiometric response slope of 59 mV/pH unit at +25 °C. But our electrodes showed lower response slope. The presence of anionic and cationic responses of the polymer film electrodes, due to the presence of ions ($\mathrm{Li}^+\mathrm{TFSI}^-$, $\mathrm{K}^+\mathrm{Cl}^-$, ions of the buffer solutions) in the different solutions probably caused this difference of response slope as suggested in the literature [9–11].

## 4. Conclusion

Platinum electrodes modified by electrosynthesized polymer films exhibit a potential response sensitive to pH changes in aqueous media. In most cases, this response appeared linear, reversible and stable in time. Moreover, the passivated platinum electrodes are not affected by the direction of the pH change. From these results we propose these polymers to be used in miniaturized analytical sensors. In particular, PPI and PPPD seem to be adequate for multi-use sensors and PANI for one-use sensor. More, we have proposed a response mechanism to pH changes of the polymeric coatings and we showed that the structures of these polymers (obtained by SEM experiments) can be use to explain the potentiometric responses to pH changes.

## Acknowledgements

We would like to thank H. Hadrien and L. Manon, for their contribution to this work and their enlightening SEM and IR–ATR analysis, respectively.

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