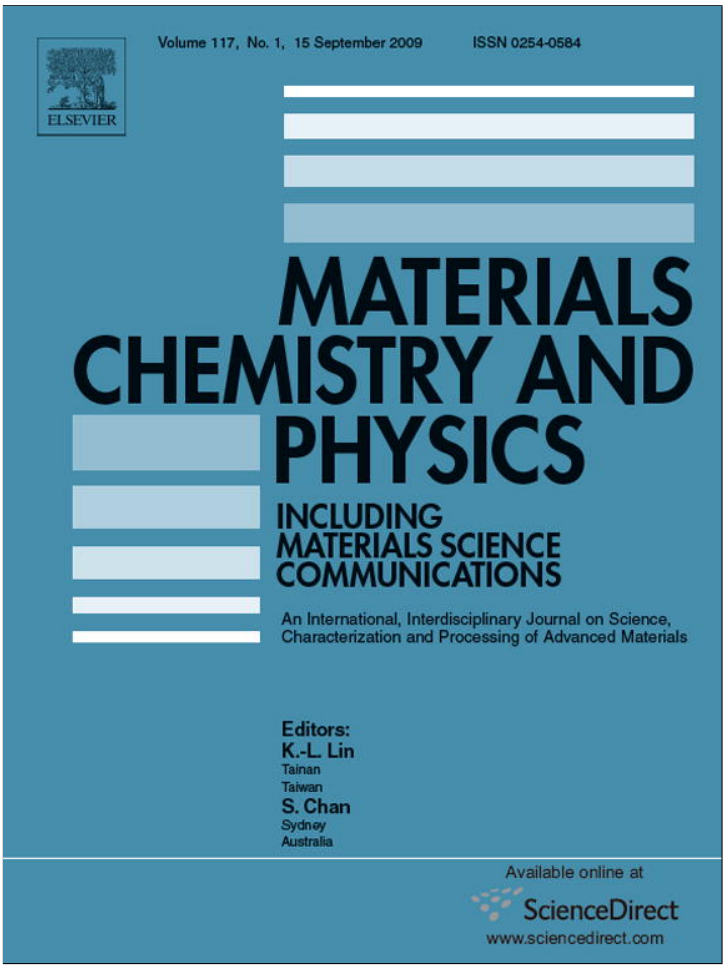


Materials Chemistry and Physics 117 (2009) 250–256

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Comparative study of polypyrrole films electrosynthesized in alkaline and acid solutions

I.L. Lehr[a], O.V. Quinzani[b], S.B. Saidman[a,*]

[a] Instituto de Ingeniería Electroquímica y Corrosión (INIEC), Departamento de Ingeniería Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina
[b] Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina

ARTICLE INFO

Article history:
Received 7 October 2008
Received in revised form 4 May 2009
Accepted 28 May 2009

Keywords:
Polypyrrole
Electropolymerization
Vitreous carbon
Acid and base treatment

ABSTRACT

The influence of the pH of electropolymerization solutions on the properties of polypyrrole films has been studied using potentiodynamic techniques and faradaic impedance spectroscopy. Scanning electron microscopy (SEM), IR and Raman spectroscopies, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were also used for products characterization. Results indicate that, contrary to what happen with the polymer electrogenerated in acid solutions, the films prepared in alkaline media are stable and present good electrochemical activity in basic solutions. Possible explanations for the observed differences are discussed and it is proposed that the pH of electropolymerization medium directly affects chains organization. Electrosynthesis in solutions of increased basicity results in a more compact and closed polymer structure.

1. Introduction

The study of the properties of polypyrrole (PPy) and its derivatives has been a subject of a large number of investigations because a wide possibility of practical applications. Electropolymerized films of these materials can be used in rechargable batteries, capacitors, anticorrosion coatings and sensors, among many other applications. Most of the studies devoted to the electrosynthesis of PPy have been carried out in organic or acid aqueous solutions. Practical applications in alkaline medium of the obtained materials are limited because basic solutions cause polymer degradation due to an irreversible loss of conjugation [1–4]. On the contrary, previous studies proved that PPy films electrosynthesized in alkaline solutions can be cycled in acid or in basic media without loosing electrochemical activity [5]. Thus, these PPy films should be suitable materials for the construction of electrodes to be used in alkaline solutions, a medium which is preferred for several important electrochemical reactions.

There are several works in the literature dealing with the electrochemical response of PPy in alkali, but there are not many relating to the electrosynthesis in this medium. Polypyrrole electrosynthesis in weakly alkaline solutions (pH 11) containing dodecylbenzenesulfonate (DBS) was reported by Shimoda and Smela [6]. Authors proposed that the negative charge of immobile DBS^- prevents OH^- attack. Solutions of pH 10.63 containing unsaturated organic sulfonate anions were used by Bhattacharya et al. [7]. It was reported that the pH of the electropolymerization solution had practically no influence on the conductivity of the film doped with styrene sulfonate, while in the case of vinyl sulfonate doped PPy, the films synthesized at higher pH had lower conductivity. Asavapiriyanont et al. showed that the cyclic voltammogram in basic solution (pH 13.2) containing pyrrole presents lower current densities compared with those obtained in acid and neutral media [8]. On the other hand, Bocchi et al. reported the electrosynthesis of PPy in strongly alkaline media [9].

As part of our investigations into PPy films electrosynthesized in alkaline media we investigated the origin of the improved performance of these films in basic media. Differentiating the factors which lead to the better performance would be helpful in controlling the properties of the films. Polypyrrole was electrosynthesized in both alkaline and acid media and the electrochemical properties of these polymers were investigated and compared using cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The films were also characterized by SEM, IR and Raman spectroscopies, TGA and DSC.

2. Experimental

Vitreous carbon rods (0.070 cm^2) embedded in a Teflon holder were used as working electrodes. Before each experiment, the exposed surfaces were polished to a 1000 grit finish using SiC, then degreased with acetone and washed with triply distilled water. All the potentials were measured against a saturated calomel electrode (SCE) and a platinum sheet was used as a counter electrode. The cell was a 20 cm^3 Metrohm measuring cell. Electrochemical measurements were done using a

* Corresponding author. Tel.: +54 291 4595182; fax: +54 291 4595182.
E-mail address: ssaidman@criba.edu.ar (S.B. Saidman).

0254-0584/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2009.05.053

potentiostat–galvanostat PAR Model 273A. A dual stage ISI DS 130 SEM was used to examine the electrode surface characteristics.

The IR spectra of the substances were recorded as KBr pellets in the 4000–400 cm^{-1} range on a Nicolet Nexus FTIR spectrometer. The Raman dispersion spectra of the solid substances in the region between 3500 and 100 cm^{-1} were obtained with a FRA 106 accessory mounted on a Bruker IFS 66 FTIR instrument, employing the 1064 nm line from a Nd-YAG laser.

The TGA analysis was carried out by a PerkinElmer thermal analyzer in the range 0–800 °C on heating the material at a constant rate of 10 °C min^{-1} in N_2 atmosphere. DSC thermograms were obtained with a TA Instrument Q20 Differential Scanning Calorimeter in the range −50 to 200 °C at a heating rate of 5 °C min^{-1} under a constant N_2 flux.

Deposition of PPy films was carried out potentiostatically at 0.90 V from solutions. The electrodeposition was done in NaCl solutions at various pH from 11 to 13.5 and in 0.1 M HCl, containing 0.15 M Py in a purified gas saturated atmosphere at 25 °C. The pH of the solution was adjusted by addition of NaOH. All chemicals were reagent grade and solutions were made in twice distilled water. Pyrrole was purchased from Sigma–Aldrich and it was freshly distilled under reduced pressure before use.

3. Results and discussion

3.1. Treatment with basic and acid solutions

Given that PPy films electrosynthesized in acid media loose their redox activity when they are immersed in an alkaline solution, treatment with acid of the PPy formed in alkaline media might result in a loss of electrochemical activity when the film is placed back in the primary electrolyte. In order to evaluate if the redox activity in alkali is degraded after acid treatment, PPy films were formed in 0.1 M NaCl solutions with different pH employing the same charge for deposition, and the redox response of the coated electrodes was examined in monomer-free alkaline and acid solutions.

Fig. 1 shows the redox process of PPy synthesized in 0.1 M NaCl, pH 11 solution containing 0.15 M Py. First, the stabilized response in the same solution without the monomer was recorded (Fig. 1, curve a). Under these conditions the exchange of Cl^- and Na^+ occurs but OH^- also participates in the redox process [5,6,10–12]. In the same figure is included the response obtained when the same electrode was transferred and potentiodynamic polarized in 0.1 M HCl solution (Fig. 1, curve b), where chloride ions enter the film to compensate the polymer charge. The redox activity in basic media was restored when the electrode was placed back into this solution (Fig. 1, curve c).

The redox activity after alternating exposure to acid and base does not disappear even if the PPy film was formed at pH 12.5. Fig. 2 shows the stabilized voltammogram of the film in 0.1 M NaCl, pH 12.5 solution (curve a). At this solution pH, the incorporation of OH^- into the polymer matrix is enhanced [5,10–12]. It can be observed

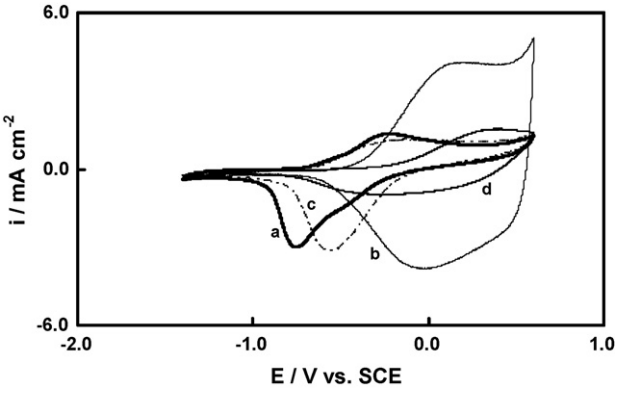


Fig. 2. Cyclic voltammograms of the PPy film at 0.05 V s^{-1} in: (a) 0.1 M NaCl, pH 12.5 solution; (b) 0.1 M HCl solution; (c) 0.1 M NaCl, pH 12.5 solution and (d) 0.03 M HCl solution. The polymer film was electrosynthesized in 0.1 M NaCl, pH 12.5 solution containing 0.15 M Py at 0.9 V for 76 s. Initial potential: 0.60 V.

that the amount of integrated charge increases when the film is cycled in acid solution (Fig. 2, curve b). The redox response does not disappear if the cyclic voltammetry was again performed in alkaline media (Fig. 2, curve c). When the voltammetric curve is recorded in 0.03 M HCl after cycling in the alkaline solution (Fig. 2, curve d) the cycled charges are very similar. Under this condition, the amount of predominant species involved in charge compensation process (Cl^- and OH^-) is the same for the two solutions (acid and alkaline).

It was not possible to obtain deposition of PPy in 0.1 M NaCl, pH 13.5 solution containing 0.15 M Py. This response can be explained considering that the high OH^- concentration hinders electropolymerization because the nucleophilic attack to radical cations. But deposition can be achieved using a higher ratio between concentrations of the monomer and OH^-. Fig. 3 shows the curves in basic and acid media obtained for a film formed in the solution of pH 13.5 containing 0.5 M Py.

Film thickness of approximately 2 μm is predicted assuming a thickness of 1 μm for 0.4 C cm^{-2} charge [13]. It should be noted that the charge involved in the redox switching decreases substantially as the solution pH increases, in spite of the same electropolymerization charge was employed. Comparing the results presented from Figs. 1–3, the charges cycled in solutions of pH 12.5 and 13.5 are 40% and 17% of that corresponding to pH 11. On the other hand, the response of the films in alkali do not change markedly after acid treatment, being the main difference the potential shift of the more cathodic peak in the positive direction for the lowest pH (pH 11).

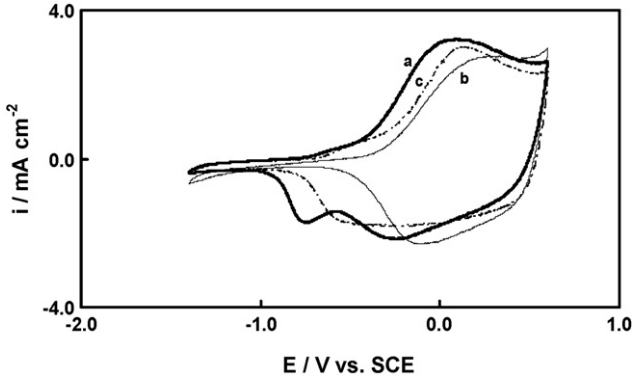


Fig. 1. Cyclic voltammograms of the PPy film at 0.05 V s^{-1} in: (a) 0.1 M NaCl, pH 11 solution; (b) 0.1 M HCl solution and (c) 0.1 M NaCl, pH 11 solution. The polymer film was electrosynthesized in 0.1 M NaCl, pH 11 solution containing 0.15 M Py at 0.9 V for 60 s. Initial potential: 0.60 V.

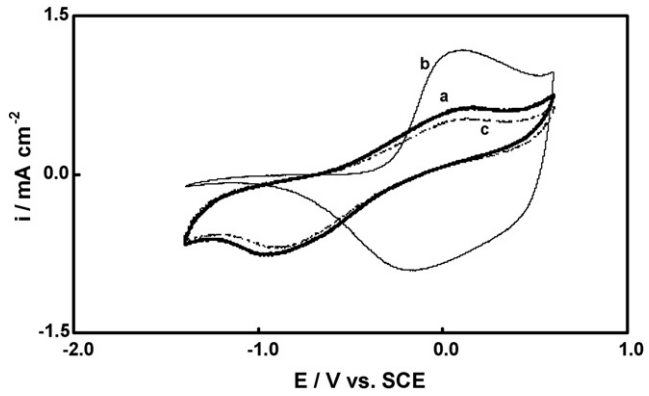


Fig. 3. Cyclic voltammograms of the PPy film at 0.05 V s^{-1} in: (a) 0.1 M NaCl, pH 13.5 solution; (b) 0.1 M HCl solution and (c) 0.1 M NaCl, pH 13.5 solution. The polymer film was electrosynthesized in 0.1 M NaCl, pH 13.5 solution containing 0.50 M Py at 0.9 V for 92 s. Initial potential: 0.60 V.

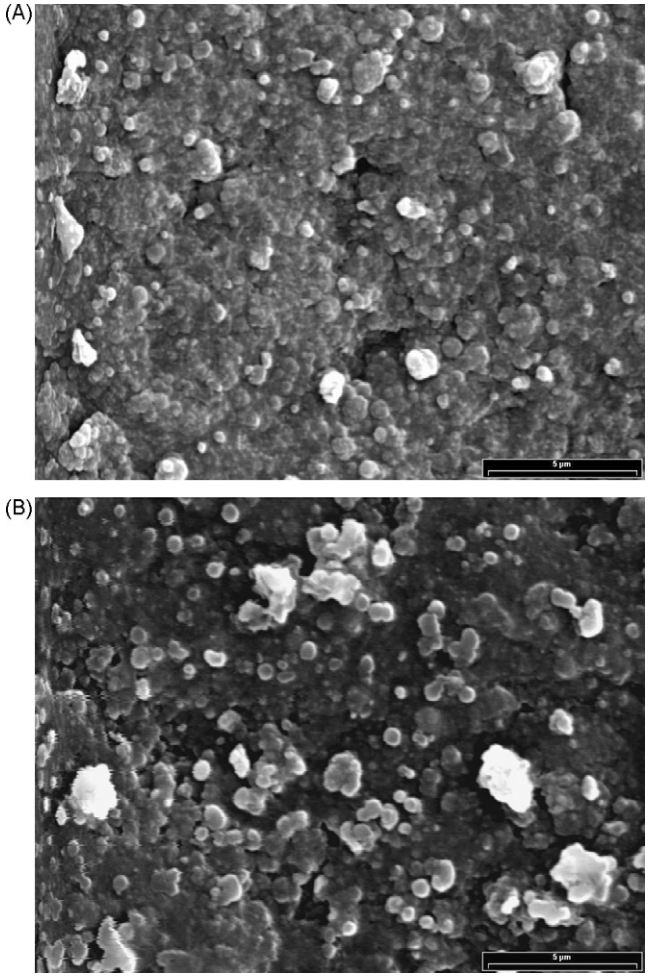


Fig. 4. SEM images of the PPy film electrosynthesized in: (A) 0.1 M NaCl, pH 12.5 with 0.15 M Py. The film was formed at 0.9 V for 7 s. (B) 0.1 M HCl with 0.15 M Py. The film was formed at 0.9 V for 5 s.

3.2. Polymer morphology

To see how the pH affects the morphology of the polymer, SEM images were obtained at the beginning of electropolymerization in 0.1 M NaCl, pH 12.5 and 0.1 M HCl solutions by using the same electropolymerization charge. For the synthesis in the alkaline solution a closely packed globular morphology is seen (Fig. 4A), while globules are more spaced for synthesis in acid media (Fig. 4B).

3.3. IR and Raman spectroscopic measurements

The polymers electrogenerated in solution of different pH were analyzed using IR and Raman spectroscopies. The vibrational spectra (IR and Raman) of the PPy films grown in 0.1 M HCl and 0.1 M NaCl, pH 13.0 solutions in the region between 1700 and 800 cm^{-1} are very similar (Figs. 5 and 6 and Table 1). Both display the vibrational bands characteristic of the oxidized state of the polymer at 1634s (IR), 1595s (R), 934s (R) and 910w (IR) cm^{-1} for the PPy films obtained in acid media [14,15]. The prominent change in the intensity of the absorption bands located below 800 cm^{-1} in the IR spectra must be assigned to a difference in the spatial disposition (packing) of the PPy chains.

A more detailed analysis of the vibrational spectra of both PPy samples shows small but significant differences. The intense band around 1590 cm^{-1} in the Raman spectra of oxidized PPy, related to a mixed υ(C=C) and inter-ring υ(C–C) vibration, appears at higher

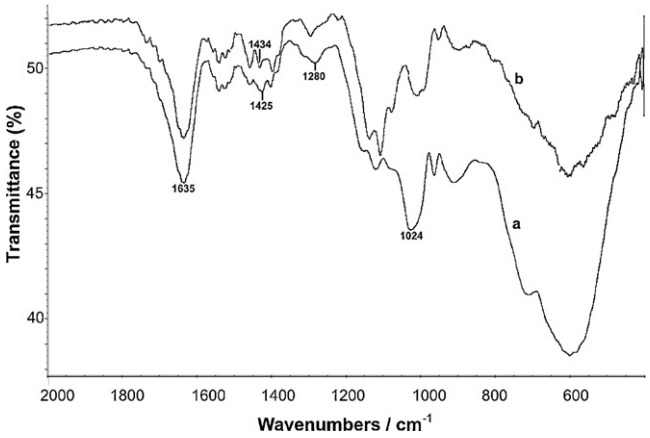


Fig. 5. Infrared spectra of PPy films deposited at 0.9 V in: (a) 0.1 M NaCl, pH 13 solution containing 0.15 M Py and (b) 0.1 M HCl solution containing 0.15 M Py.

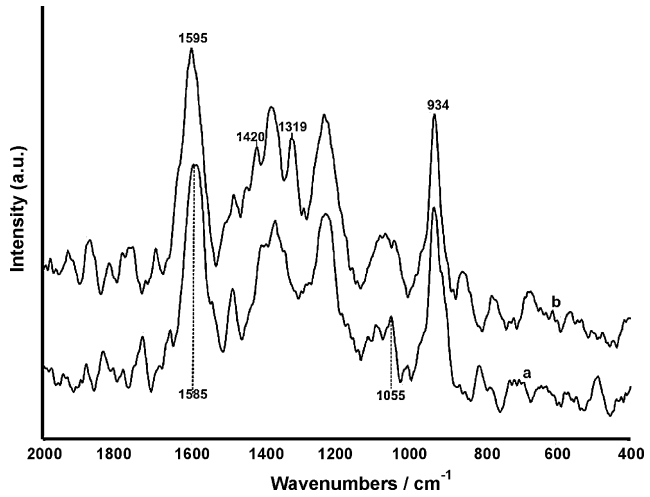
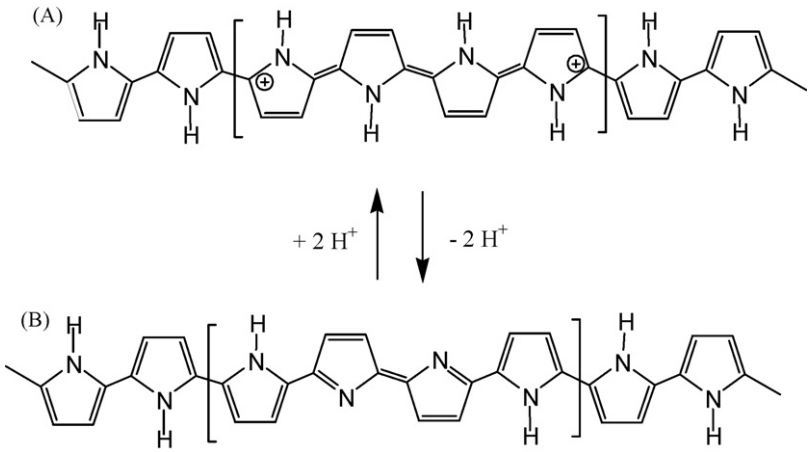


Fig. 6. Raman spectra of PPy films deposited at 0.9 V in: (a) 0.1 M NaCl, pH 13 solution containing 0.15 M Py and (b) 0.1 M HCl solution containing 0.15 M Py.

Table 1
Selected IR and Raman bands (cm^{-1}) of the polypyrrole films electrosynthesized in alkaline and acid media.

Polypyrrole films				
1.0 M NaCl (pH 13.0)		1.0 M HCl		Assignments[a]
IR	Raman	IR	Raman	
1635s[b]		1634s		υ(C=C)
	1585s		1595s	υ(C=C) + υ(C–C) bridge
1540w		1540w		υ(C=N)
	1483w		1483w	υ(C=N)
1456w		1460 w		υ(C=C)
1425w		1434w		υ(C=C) + υ(C–C) bridge
	1404sh		1420w	υ(C=C)
	1369m		1378m	υ(C=C)
	–		1319w	υ(C=C) bridge
1311w		1303w		υ(C=N)
1280w		–		υ(C=C)
	1230m		1234m	υ(C=C)
1152w		1151w		δ(C–H)
1119s		1123s		υ(C–C)
	1089w		1067w	δ(C–H)
	1055m		1052w	δ(C–C) bridge
1024s		1020m		δ(C–H)
	933s		934s	δ(CCC)
900w		903w		δ(C–H)
580vs, br		595vs, br		PPy chain

[a] See text.
[b] br: broad, m: medium, s: strong; sh: shoulder, vw: very weak, w: weak.



Scheme 1. Protonation–deprotonation model for polypyrrole chains.

wavenumbers in the polymer prepared in acid media (1595 cm^{-1}) than in the films obtained in alkaline solutions (1585 cm^{-1}). The band assignable to a stretching motion of the inter-ring C—C bonds (1055m cm^{-1}) has high intensity in the latter than in the former. The Raman spectrum of the film prepared in acid solution presents two weak bands centred at 1420 and 1319 cm^{-1}, while these bands are less intense or absent in the spectra of the polymer synthesized in basic medium. The band at 1420 cm^{-1} is assigned to a C=C stretching of the pyrrolic rings, and the band at 1319 cm^{-1} to a C=C stretching of reinforced inter-ring bonds [14]. In addition, the 1434 cm^{-1} band in the IR spectra of the PPy polymerized in acid media moves to lower wavenumbers (1422 cm^{-1}) in the spectra of the polymer formed at the higher pH. The whole observed changes between the vibrational spectra of the two PPy indicate that in the film prepared at lower pH the polymeric chains are slightly richer in unsaturated C=C inter-ring bonds and in less unsaturated pyrrolic rings, which correspond to a high oxidized form of the polymer [14,15]. This pH-dependent behaviour of the polymer agrees with the protonation–deprotonation model for the polypyrrole chains already described [16] and reproduced in Scheme 1. The structure with positively charged pyrrolic rings and unsaturated C=C bridges (structure A) requires planarity of the system and, as a consequence, polymer chains with high rigidity are produced. When a PPy prepared is synthesized in alkaline media, the structure of the PPy chains change to a new form with increased contribution of saturated C—C bridges and of fully unsaturated pyrrolic rings (structure B). This type of structure, poorer in terms of conjugation, allows a twisted chain conformation.

3.4. Redox response of films formed in alkaline solution at different temperatures

Further information may be gained from the redox curves of the polymer electrosynthesized at different temperatures. Films were prepared in the range of 5–40 °C at 0.9 V in 0.1 M NaCl, pH 12.5 solution containing 0.15 M Py. The rate of growth of the polymer was increased when the electropolymerization temperature was higher. The cyclic voltammograms of the films were performed in a Py-free solution at 20 °C. One clearly notices from Fig. 7 that the cycled charge increases as the electropolymerization temperature decreases. Since the charge consumed during polymerization was the same, the doping level increases as the temperature decreases, in accordance with other works [17]. Another explanation may be that higher electropolymerization temperatures promote the occurrence of side reactions which consume charge without producing electroactive polymer [18]. Successive scans resulted in a gradual negative shift in the anodic peaks, whereas the cathodic

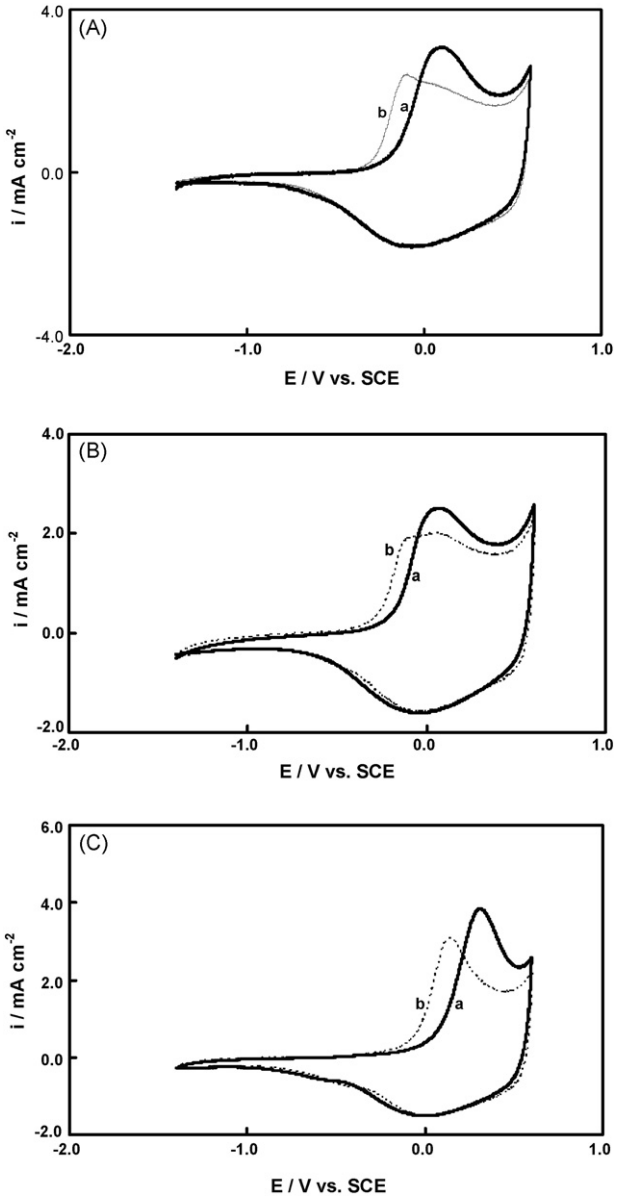


Fig. 7. Cyclic voltammograms of PPy films at 0.05 V s^{-1} in 0.1 M NaCl, pH 7 solution. The polymer films were electrosynthesized at 0.9 V in 0.1 M NaCl, pH 12.5 solution containing 0.15 M Py at: (A) 5 °C, for 60 s; (B) 20 °C, for 50 s; (C) 40 °C, for 38 s. Initial potential: 0.60 V. (a) Scans 1 and (b) 5 are displayed.

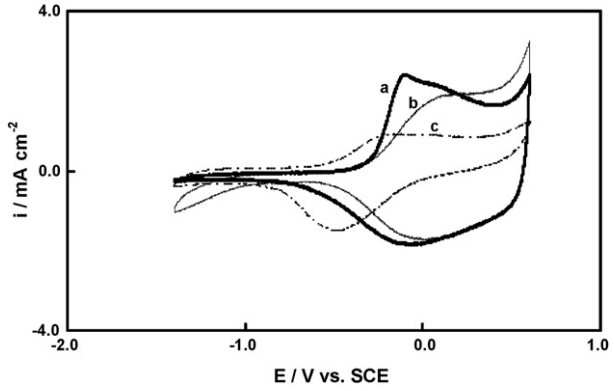


Fig. 8. Cyclic voltammograms of the PPy film at 0.05 V s^{-1} in: (a) 0.1 M NaCl, pH 7 solution; (b) 0.1 M HCl solution and (c) 0.1 M NaCl pH 12.5 solution. The polymer films were electrosynthesized at 5 °C in 0.1 M NaCl, pH 12.5 solution containing 0.15 M Py at 0.9 V for 60 s. Initial potential: 0.60 V.

waves remain practically unchanged. For the lower electrosynthesis temperatures, the broad anodic peak is transformed in two distinct peaks. The charge of the peak at the more negative potentials increases until a stable response is obtained. On the other hand, the peak at the more negative potentials becomes more evident as the temperature employed during polymerization was lower.

For the sake of comparison, the polarization curve obtained when the polymer formed in alkaline solution at 5 °C is cycled in neutral pH (curve a) is superimposed on curves b and c in Fig. 8, which show the behaviour of comparable films in chloride solution of pH 12.5 and 0.1 M HCl, respectively.

3.5. Prolonged exposure to alkaline solution

The stability of the film formed in basic solution upon exposure to alkaline medium for prolonged times was evaluated by means of cyclic voltammetry and EIS. Cyclic voltammograms were registered after different immersion periods (Fig. 9). The film can be cycled between the conducting and insulating state without decomposition. With increasing immersion time a more resistive response is observed, and a redox process appears at the more positive potentials, which is probably due to Cl^- exchange. On the contrary, when the film exposed to the alkaline medium was formed in an acid solution, the total charge decreases markedly during the first cycles until the redox ability of the film almost disappeared [3,5].

Nyquist and Bode plots of PPy films for different immersion times are presented in Fig. 10. The feature of all the Nyquist plots

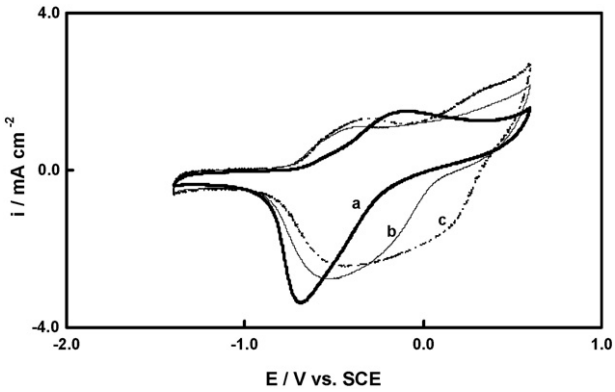


Fig. 9. Cyclic voltammograms of the PPy film at 0.05 V s^{-1} in 0.1 M NaCl, pH 12.5 solution for different times of immersion: (a) 0 h; (b) 24 h; (c) 48 h. The polymer film was electrosynthesized in the same solution containing 0.15 M Py at 0.9 V for 3 min.

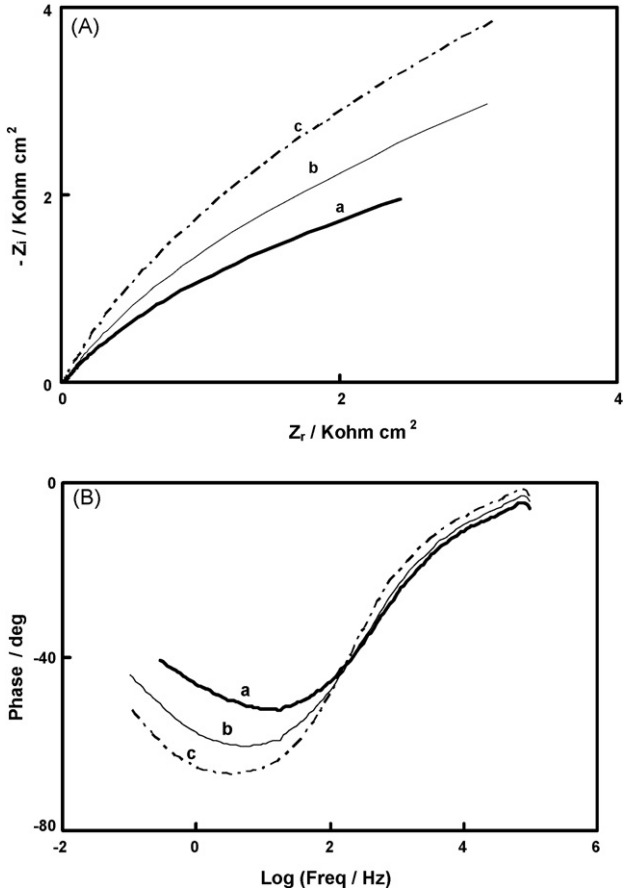


Fig. 10. (A) Nyquist and (B) Bode plots of the impedance spectra for the PPy film at 0.50 V in 0.1 M NaCl, pH 12.5 for different times of immersion: (a) 0 h; (b) 24 h; (c) 48 h. The polymer film was electrosynthesized in the same solution containing 0.15 M Py at 0.9 V for 3 min. The frequency was varied between 100 KHz and 100 mHz.

was a depressed semicircle which diameter increases as function of time (Fig. 10A). The impedance spectrum of a polymer-coated electrode in contact with an electrolyte solution can be interpreted in terms of a simple equivalent circuit based on the electrolyte resistance (R_s) in series with a capacitance (C_g) and a bulk resistance (R_b) in parallel with C_g [19]. The R_b term represents the resistance of PPy and C_g is associated with the charging capacitance of the film.

The increase of R_b with time can be ascribed to a deactivation of the polymer by overoxidation degradation. But the possibility of overoxidation can be ruled out since the redox exchange properties of the polymer remains practically unaltered. The diagrams present similar characteristics when the film was taken out of the basic solution and placed into acid solution and even by exposing again to alkali. The increase in R_b observed through exposure can be due to a disruption of conduction pathways as the prevailing result of swelling.

3.6. Thermal stability

The TGA curves of PPy formed in alkaline and acid electrolytes are presented in Fig. 11. The decomposition curves are similar to those described for other authors [20,21]. The first weight loss from room temperature to 105 °C is associated with the evaporation of residual water and then both samples gradually lost their weights due to a complex decomposition process. The residual percentages of PPy formed in NaCl, pH 12.5 and HCl after the TGA analysis (800 °C) are 62% and 58%, respectively.

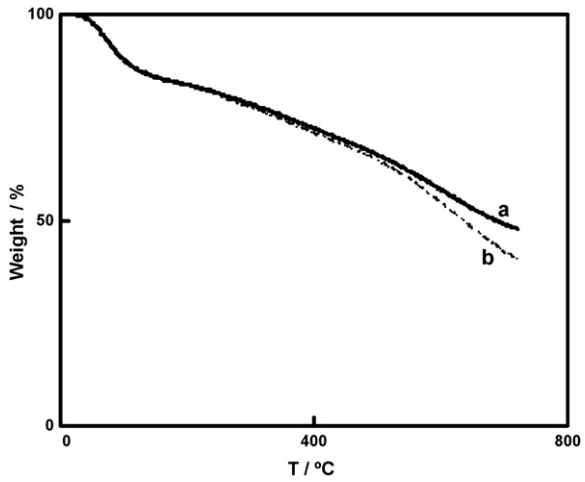


Fig. 11. TGA curves obtained at 10 °C min^{-1} under nitrogen for PPy-coated CV electrode. The polymer films were electrosynthesized in: (a) 0.1 M NaCl, pH 12.5 solution with 0.15 M Py and (b) 0.1 M HCl, solution with 0.15 M Py.

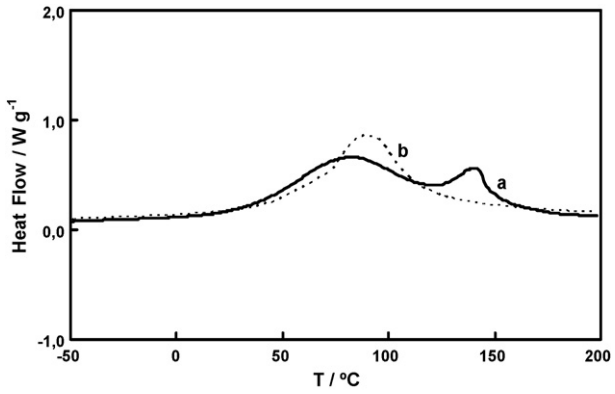


Fig. 12. DSC curves obtained at 5 °C min^{-1} under nitrogen for PPy films electrosynthesized in: (a) 0.1 M NaCl, pH 12.5 solution with 0.15 M Py and (b) 0.1 M HCl, solution with 0.15 M Py.

Fig. 12 shows the DSC curves over a temperature range before polymer decomposition initiates. DSC trace for the polymer synthesized in acid solution shows essentially one endothermic peak while two peaks are observed for the polymer deposited in alkaline medium. Considering that PPy prepared electrochemically does not show glass transition due to the rigid chains and cross-linkage [21], and as far as we know, these curves should correspond to the removal of residual water. Although no definitive explanation can be presented for the endothermic peaks, the difference between both DSC curves clearly indicates that the structures of the polymers are not the same.

4. Discussion

The present results indicate that PPy films with good cyclability were formed in alkaline solutions. Likewise, the electrochemical activity in basic media remains practically unchanged after immersion in acid solution. By comparing the results presented from Figs. 1–3, it can be concluded that the polymerization efficiency decreases as the solution pH increases. This result can be explained considering that the proportion of chain segments with structure B (Scheme 1) increases as the solution pH increases.

There are many factors such as pH, nature of solvent and dopant ions, temperature, which can influence the electropolymerization of PPy and consequently the structure of the polymer. Thus, several structures of PPy have been described. The existence of two doping structures for PPy electrosynthesized in aqueous media was proposed [13]. It was postulated that PPy chains has some pyrrole units which lost electrons to the electrode and some units which are protonated. Both will lead to a positively charged chain. The results of the present work seem to be consistent with the existence of the described structures. That is, the regular polymer and the protonated form of PPy can be formed depending on the pH of the electropolymerization solution. It is expected that the continuous generation of protons during polymerization in alkaline media does not lead to polymer protonation. Although in alkaline media protons are generated during electropolymerization, the pH value at the interface will not be different from that of the bulk solution. Then, alkaline solutions prevent the formation of oligopyrrole units that contain protonated centers.

In spite of protonation is expected to take place in acid media, the IR and Raman studies of PPy samples synthesized in acid solution do not allow confirming the presence of protonated chains in the film. This was also observed by other authors [22], who proposed that protonation occurs without formation of localized bands.

It was also reported that two forms of PPy, PPy(I) and PPy(II), can be prepared in non-aqueous solution under controlled conditions [23,24]. While PPy(II) consists of relatively short oligopyrrole units, PPy(I), which is the regular polymer, contains longer chains. A lower polymerization temperature increases the fraction of PPy(II) and the conductance of the films. PPy(II) contains localized protonic charges on the oligomeric chains and anions are strongly bound to the positively charged sp^3 center. It was proposed that, in spite of acid was not present initially in the electrolyte, some trace amounts of hydrogen ions may appear as a result of the deprotonation of the monomeric Py units during electrolysis [25]. On the other hand, PPy(II) can be formed at low proton concentration (10^{-5} M) in acetonitrile. The two forms of PPy can be distinguished in cyclic voltammetry, where the oxidation peak at the more negative potentials indicates the presence of PPy(II). Our measurements presented in Fig. 7 are very similar to the cyclic voltammograms described for PPy films synthesized in organic media. Then, we propose that when the PPy films synthesized in basic solution are repeatedly cycled in neutral media, short oligopyrrole units can be protonated and then the anodic peak at the more negative potentials appears during cycling. The proportion of localized protonic charges increases as the electropolymerization temperature decreases.

The results presented here indicate that when OH^- ions act as dopants they modify the PPy structure, protecting the polymer backbone from nucleophilic attack. DSC analysis confirms that the structures of the polymers are not the same. The obtained films maintain their electrochemical activity when they were immersed in basic media even after long periods of exposure (Fig. 9). Only a slight film swelling was observed.

In order to explain an improvement of long-term term stability of the conductivity of PPy after soaking in alkaline solutions it was postulated that OH^- forms covalent bonds with PPy [26]. But this explanation is ruled out since there is no signal of OH in the IR spectra.

As was discussed above, the concentration of positive charges on the chains is lower for the polymer in alkaline solution with respect to that synthesized in acid media: (i) there are not protonated units and (ii) there is a higher proportion of segments in the chain with structure B. As a result attractive coulombic forces between neighbouring polymer chains are stronger, decreasing the interchain distances. In addition, polymer chains with less rigidity are formed at the higher pH. Thus, the polymer electrosynthesized in alkaline solutions adopts a more compact and closed morphology accompanied with a slight loss of charge delocalization. All these factors contribute to difficult the nucleophilic attack by OH^-.

It was proposed that more Py units will be protonated after acid treatment of PPy [3,13,22]. On the other hand, according to earlier

considerations, a facilitated transport of ions is expected in acid media because the more open structure. But an increased cycled charge was not observed when the film synthesized in alkaline solution was immersed in acid medium (Fig. 2). We can conclude that the film electrosynthethized in alkaline solution not only is protected from OH^- attack but also the formed structure cannot be protonated after treatment in acid. This behaviour explains why the electrochemical activity of these films is not degraded after acid treatment.

5. Conclusions

Polypyrrole films obtained by potentiostatic polymerization in alkaline media are stable and exhibit good cyclability in solutions with high pH. From the experimental results mentioned above our proposition is that, in spite of the conjugated double bond in the polymer is not destroyed when the film is electrosynthesized in alkaline solutions, there are more segments in the chain where the conjugation is broken. Moreover, there are not protonated units in the chains. All this leads to less rigid chains with less positive charges, and therefore a more compact and closed polymer structure is formed. This structure would protect the polymer backbone from nucleophilic attack by OH^- during exposure to alkaline solutions.

The closed structure of the films prepared in alkaline solutions remains unchanged during cycling voltammetry in acid solution, indicating that protonation is unfavourable.

Acknowledgement

CONICET, ANPCYT and Universidad Nacional del Sur, Bahía Blanca, Argentina are acknowledged for financial support. We also want to thank Dr. J.A. Güida (CEQUINOR, UNLP) for recording the Raman spectra.

References

[1] S. Kuwabata, J. Nakamura, H. Yoneyama, J. Electrochem. Soc. 137 (1990) 2147.
[2] P. Novak, B. Rasch, W. Vielstich, J. Electrochem. Soc. 138 (1991) 3300.
[3] M. Hepel, Electrochim. Acta 41 (1996) 63.
[4] L. Liu, Y. Zhao, N. Jia, Q. Zhou, Ch. Zhao, M. Yan, Z. Jiang, Thin Solid Films 503 (2006) 241.
[5] S.B. Saidman, Electrochim. Acta 48 (2003) 1719.
[6] S. Shimoda, B. Smela, Electrochim. Acta 44 (1998) 219.
[7] A. Bhattacharya, A. De, S. Das, Polymer 37 (1996) 4375.
[8] S. Asavapiriyanont, G.K. Chandler, G.A. Gunawardena, D. Pletcher, J. Electroanal. Chem. 177 (1984) 229.
[9] V. Bocchi, G.P. Gardini, G. Zanella, Synth. Met. 41–43 (1991) 3067.
[10] Y. Li, R. Qian, G. Zanella, Synth. Met. 26 (1988) 139.
[11] Y. Li, R. Qian, G. Zanella, Synth. Met. 28 (1989) C127.
[12] Y. Li, Z. Liu, Synth. Met. 94 (1998) 131.
[13] Q. Pei, R. Qian, Electrochim. Acta 37 (1992) 1075.
[14] M.J.L. Santos, A.G. Brolo, E.M. Girotto, Electrochim. Acta 52 (2007) 6141.
[15] H. Nguyen Thi Le, M.C. Bernard, B. Garcia-Renaud, C. Deslouis, Synth. Met. 140 (2004) 287.
[16] Q. Pei, R. Qian, Synth. Met. 45 (1991) 35.
[17] W. Liang, J. Lei, Ch.R. Martin, Synth. Met. 52 (1992) 227.
[18] J. Ouyang, Y. Li, Synth. Met. 79 (1996) 121.
[19] C. Fernández-Sánchez, C.J. McNeil, K. Rawson, Trends Anal. Chem. 24 (2005) 37.
[20] Y.C. Liu, J.M. Huang, Ch.E. Tsai, T.C. Chuang, Ch.C. Wang, Chem. Phys. Lett. 387 (2004) 155.
[21] N. Li, D. Shan, H. Xue, Eur. Polym. J. 43 (2007) 2532.
[22] E. Sánchez de la Blanca, M.I. Redondo, M.V. García, M.A. Raso, J. Tortajada, M.J. González-Tejera, Synth. Met. 139 (2003) 145.
[23] M. Zhou, M. Pagels, B. Geschke, J. Heinze, J. Phys. Chem. B 106 (2002) 10065.
[24] C.C. Bof Bufon, J. Vollmer, T. Heinzel, P. Espindola, H. John, J. Heinze, J. Phys. Chem. B 109 (2005) 19191.
[25] Y.S. Cohen, M.D. Levi, D. Aurbach, Langmuir 19 (2003) 9804.
[26] H. Münstedt, Polymer 27 (1986) 899.