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Characterisation of polypyrrole electrosynthesised on aluminium

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Abstract

Cyclic voltammetry has been used to investigate the role of the anions and the solution pH on the redox properties of polypyrrole electrosynthesised onto aluminium in alkaline solutions. The polymer film was characterised by SEM and IR spectroscopy. Moreover, the influence of the cathodic potential on the redox process was analysed for films formed in acid and alkaline solutions. The electrochemical response was compared with that obtained on vitreous carbon electrode. The differences in the shape and evolution of the voltammograms during cycling have been explained by a different participation of the ions. The best redox activity of the polymer is obtained in NO_3^- due to the fact that this anion could limit the anodic dissolution of Al. The other anions analysed cannot be incorporated into the polymer matrix. As a consequence, the transport of OH^- occurs, which provokes a significative Al dissolution. It is expected that the Al^{3+} ions generated during the electrodissolution are incorporated into the polymer in order to equilibrate the charge of the film.

Keywords: Aluminium electrode; Polypyrrole; Electrodeposition; Cyclic voltammetry; Ion exchange

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1. Introduction

In the last years, a great interest has been paid to the electrodeposition of conducting polymers onto active metals due principally to their use as anti-corrosion coatings [1]. Several authors have reported significant results in the synthesis of polypyrrole (PPy) onto reactive metals such as Al [2–10]. In a previous publication the possibility of obtaining conductive and adherent PPy films on Al in NO_3^--containing solution of pH 12 has been demonstrated [8]. The influence of pH on the electropolymerisation of Py onto Al electrodes was explained considering that the passive layer formed might be able to inhibit the dissolution of the metal without blocking the access of the monomer and its further oxidation. No film formation was observed in neutral and weakly alkaline solutions because the oxide passivates the electrode and hinders the process of polymerisation. As the solution pH is raised, the oxide layer become less protective allowing the electropolymerisation at pH 12. Further increase in pH results in a suppression of the polymerisation process due to the high rate of Al dissolution. The best quality films are produced potentiostatically at pH 12 in the potential range 0.70–1.10 V. Deposition starts after the oxidation and passivation of Al occur. The passive film has many defects and the nucleation of the polymer starts at these sites. There is evidence to suggest that the passive film is less protective than the one formed at acid pH, and, consequently, a greater number of defects are available for polymer nucleation at pH 12 [8]. The films can be cycled in acid solution without loosing its redox behaviour.

On the other hand, PPy films have been prepared on vitreous carbon in alkaline solutions [11]. The films show variable ion-exchange properties, which depend strongly on the nature of the counter-anion and solution pH. During the redox process the transport of anions like NO_3^- or Cl^- is dominant, although the exchange of OH^- also occurs. Cation transport also takes place to compensate the incomplete release of NO_3^- or Cl^-. In the case of SO_4^{2-}, the exchange of OH^- exclusively occurs during the redox process. In this pa-

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per the electrodeposition of PPy coatings on Al from SO_4^{2-} solution was investigated.

A reduction process at very negative potentials was associated with the transport of the cations for PPy films formed onto vitreous carbon [11]. With this in mind, the voltammetric behaviour of PPy formed onto Al was examined by extending the voltage in the cathodic region.

Another objective of the present work was to get a better knowledge of the properties of PPy electrosynthesised on Al in alkaline solutions. In this sense, the earlier work was extended by analysing the role of pH and anions on the redox process.

The influence of the Al oxide on the electropolymerisation process and on the redox response of the formed film was analysed by comparing the results obtained with Al and with vitreous carbon.

The films were also characterised by SEM and IR spectroscopy.

2. Experimental

Aluminium (99.999%, Aldrich Chemical Company) and vitreous carbon (The Electrosynthesis Co.) rods embedded in a Teflon holder with an exposed area of 0.070 cm^2 were used as working electrodes. Before each experiment, the electrode was polished successively with 200, 600 and 1000 emery paper, then degreased with acetone and washed with triply-distilled water. Following this pretreatment, the electrode was immediately transferred to the electrochemical cell. 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 and measurements were done in a purified nitrogen gas saturated atmosphere at 25 °C.

Solutions of different salts as $NaNO_3$, Na_2SO_4, $Na_2C_2O_4$ (sodium oxalate), $NaCH_3CO_2$ (sodium acetate) and acids, HNO_3 and H_2SO_4 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. Pyrrole was purchased from Acros Organics and it was freshly distilled under reduced pressure before use.

Electrochemical measurements were done using a linear voltage sweep generator PAR model 175, a potentiostat-galvanostat PAR model 173 and HP 4007 B *x*–*y* recorder. Scanning electronic microscopy pictures were taken with a Jeol 100. Infrared spectra were recorded with a Nicolet Nexus FTIR spectrophotometer, using the KBr pellet technique.

3. Results and discussion

3.1. Redox behaviour of PPy with various electrolyte anions

Electroactive films were prepared by electropolymerisation of Py at a constant potential of 0.90 V for 30 s in 0.1 M NO_3^-, pH 12 solution containing 0.5 M Py. Fig. 1 shows the redox behaviour of the films synthesised on both vitreous carbon and Al. The consumed charge during deposition was 37.0 and 77.5 mC for Al and vitreous carbon, respectively. This difference can be explained by the presence of the oxide film in the case of Al. In both cases the inserted NO_3^- anions are expelled from the film at the beginning of its reduction [11]. The observed redox peaks in the −0.5–0.3 V range are associated with the exchange of NO_3^-. A positive shift of the peak potentials can be observed for the PPy-covered Al electrode compared with those obtained for vitreous carbon. Moreover, the separation between the peak potentials is smaller when the substrate is vitreous carbon, indicating that in this case is easier to oxidise and reduce the film. This difference might be explained considering the additional resistance of the Al oxide film.

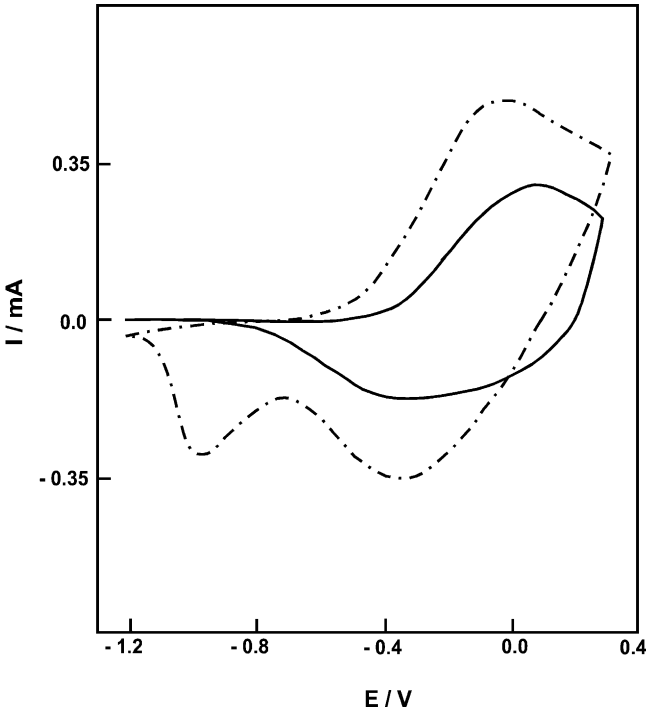

Fig. 1. Stabilised cyclic voltammograms of PPy on Al (full line) and vitreous carbon electrode (discontinuous line) in 0.1 M NO_3^-, pH 12 solution at 0.05 V s^{-1}. The film was made potentiostatically (E = 0.90 V, t = 30 s) in 0.1 M NO_3^-, pH 12 solution containing 0.5 M Py.

Another important difference in the behaviour of both substrates is the absence of the more cathodic peak (−0.95 V) in the case of Al. This peak is absent in acid media but it can be observed in neutral and alkaline solutions, where its charge is pH independent [11]. While a dependence on the cation was found, the shape and potential of the peak are practically independent of the anion. Thus, this peak was attributed to the compensation of the polymer charges by Na^+ insertion when the film is formed on vitreous carbon. This result suggests that transport of Na^+ does not contribute to the redox process when the substrate is Al. The integrated charge under oxidation and reduction waves associated with the redox process of the polymer are very similar. Thus, the coulombic efficiency is ca. 100%. In the case of Al, these charges were obtained by the difference between the total current on the cyclic voltammogram and the current obtained with an uncovered electrode. A possible explanation of the absence of the peak related to the Na^+ insertion when the film is formed on Al is that the Al^{3+} (or $Al(OH)_4{}^-$) ions generated during dissolution are also able to contribute to the ion exchange process and then, the Na^+ ions are no longer necessary to conserve the electroneutrality of the film when the PPy is reduced to its neutral state. Aluminium ions generated by the electrochemical oxidation can also be involved in a film-formation process resulting in Al_2O_3, or in a dissolution process resulting in soluble species which migrate into the bulk of the solution [5]. The Al^{3+} ions would be expelled from the polymer during the oxidation process of the film.

Information of the morphology of the polymer formed on Al substrate in $NO_3{}^-$solution can be obtained from the scanning electron microscopy technique as featured in Fig. 2. SEM image of a film deposited at 0.90 V shows a globular structure with the formation of aggregates, similar to that obtained in acid media [7]. It is interesting to note that in alkaline media a closely packed globular morphology is observed in contrast with the film synthesised in acid solution where the globules are more spaced.

The polymer generated on Al in the oxidised state was also analysed using IR spectroscopy. The film was scraped off the electrode, ground to a fine powder and analysed as KBr pellets. No attempt has been made to assign all the peaks, but it is worthwhile to note the presence of a strong and sharp band at 1386 cm^{-1} and a weak band at 834 cm^{-1} (Fig. 3a) attributed to stretching vibrations of the $NO_3{}^-$ anions, $\nu_3(NO_3{}^-)$ and $\nu_4(NO_3{}^-)$, respectively [12]. Thus, this result shows a clear sign of the presence of $NO_3{}^-$ as a dopant. No peak at ca. 1700 cm^{-1} attributed to a C=O structure is observed, indicating that the formed polymer is not irreversibly degraded. The peak at 1630 cm^{-1} should be assigned to C=C bond stretching of the pyrrole ring. The bands at 1165 and 1029 cm^{-1} correspond to C–H bonds deformations and the band at 1120 cm^{-1} can be assigned to the breathing vibration of the pyrrole ring.

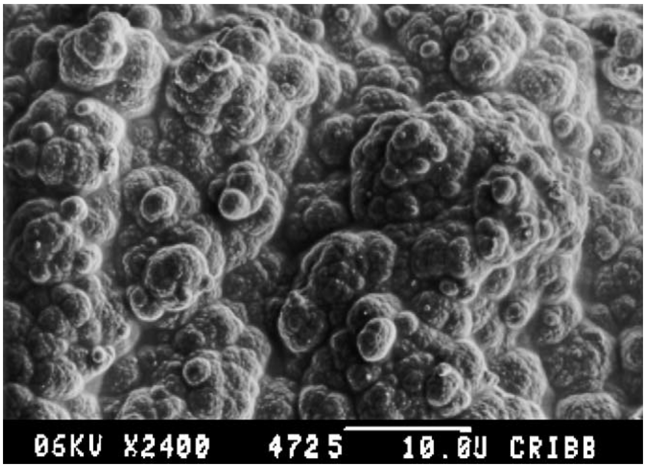

Fig. 2. SEM micrograph of PPy-coated Al. The film was formed at 0.90 V in 0.1 M $NO_3{}^-$, pH 12 solution containing 0.5 M Py.

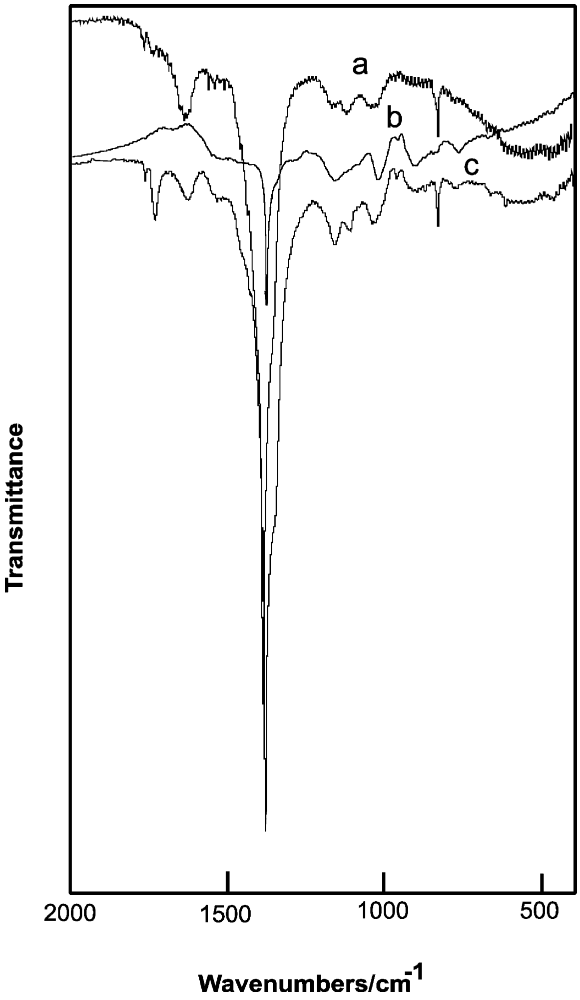

Fig. 3. Infrared spectra of (a) PPy deposited on Al at 0.90 V in 0.1 M $NO_3{}^-$, pH 12 solution containing 0.5 M Py; (b) the film formed in (a) maintained at −1.00 V in 0.1 M $NO_3{}^-$, pH 12 solution for 15 min; (c) the film formed in (a) maintained at 1.20 V in 0.1 M $NO_3{}^-$, pH 12 solution for 15 min.

The intensity of the peak at 1386 cm^{-1} diminishes and the band at 834 cm^{-1} disappears when the PPy film is electrochemically reduced (Fig. 3b). Despite its weaker intensity, the presence of the first band in the spectrum of the reduced form indicates an incomplete release of $NO_3{}^-$, as was previously suggested [11]. The IR spectrum shows the absence of the absorption bands at 1630 and 1120 cm^{-1}. This result can be attributed to the different electronic configuration on the pyrrole ring between the oxidised and reduced forms. The bands at 1165 and 1029 cm^{-1} remain almost unchanged because the C–H bonds are slightly affected during reduction of the pyrrole ring.

When the PPy-covered Al electrode was cycled in a 0.1 M $NO_3{}^-$ solution, pH 12, an irreversible oxidation current peak appeared at ca. 1.20 V [8]. The IR spectrum of a film polymerised from 0.1 M $NO_3{}^-$ pH 12 solution containing 0.5 M

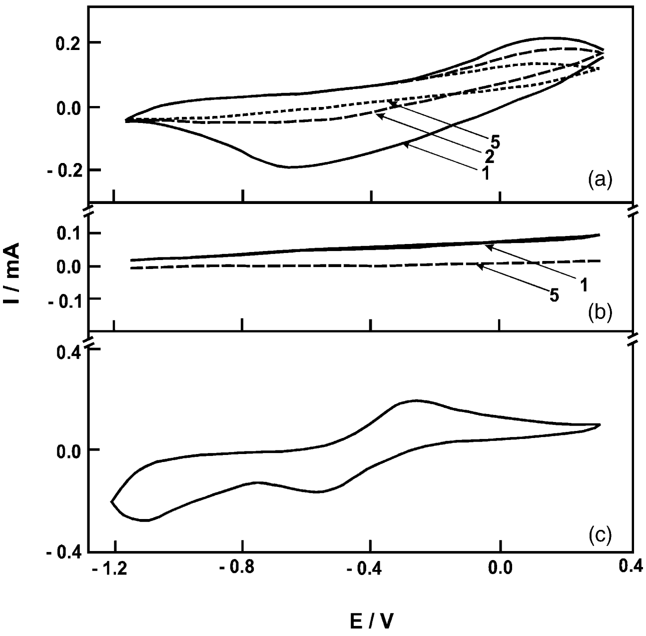

Fig. 4. Cyclic voltammograms in 0.01 M NaOH solution at 0.05 V s^{-1}. (a) PPy-coated Al electrode (b) bare Al and (c) PPy-coated vitreous carbon electrode (stabilised *I*/*E* curve). The PPy films were made potentiostatically (E = 0.90 V, t = 30 s) in 0.1 M NO_3^-, pH 12 solution containing 0.5 M Py. The cycle numbers are indicated. Initial potential: 0.30 V.

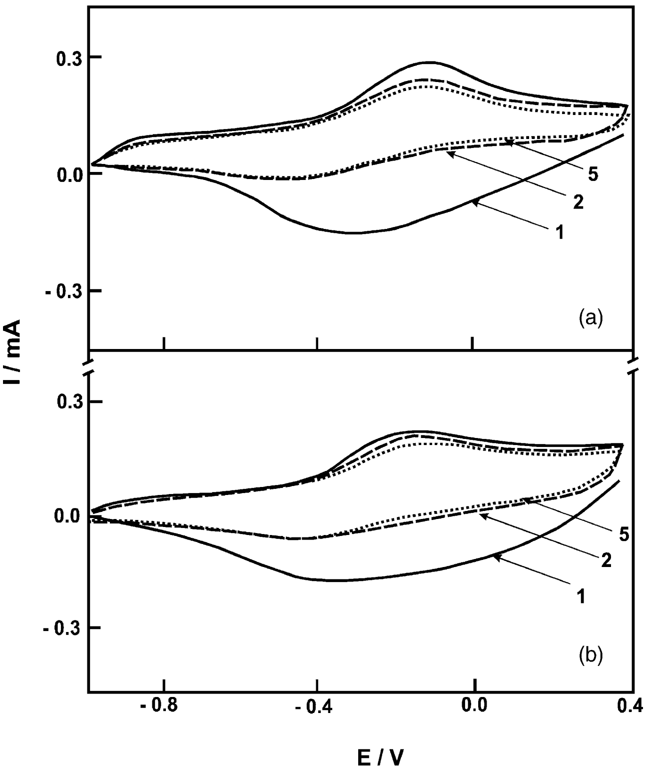

Fig. 5. Cyclic voltammograms of PPy-coated Al electrode in (a) 0.1 M CH_3COO^-, pH 12 solution and (b) 0.1 M $C_2O_4^{2-}$, pH 12 at 0.05 V s^{-1}. The film was made potentiostatically (E = 0.90 V, t = 30 s) in 0.1 M NO_3^-, pH 12 solution containing 0.5 M Py. The cycle numbers are indicated.

Py and maintained at 1.20 V in a monomer-free solution for 15 min is shown in Fig. 3c. As compared to the spectrum of the polymer shown in Fig. 3a, there are only weak changes, except that a new peak arises at 1734 cm^{-1}, which is ascribed to the formation of the carbonyl group. This result confirms the polymer was degraded. The intensity of the peak at 1630 cm^{-1} is reduced upon polymer degradation. The presence of the NO_3^--absorption band indicate that only some pyrrole rings in the PPy chain were degraded after this overoxidation time, originating a partial removal of doping anions.

The nature of the supporting electrolyte used for the cycling of the resulting polymer on Al was also investigated. PPy films synthesised in NO_3^- were submitted to voltammetric studies in solutions with different electrolytes. First, the electrochemical behaviour in 0.01 M NaOH was evaluated (Fig. 4a). For comparison, the potentiodynamic curve recorded for a bare Al (Fig. 4b) and the electrochemical response of PPy synthesised under similar conditions on vitreous carbon (Fig. 4c) are included in the same figure. As occurs with vitreous carbon, expulsion of the original counteranion takes place on the first reduction scan [11]. It can be observed that in the absence of NO_3^- the redox activity decreases and the voltammetric response of the polymer is included within a large anodic current. As a result, the voltammetric curve obtained with the PPy-covered electrode is very similar to that obtained with the uncovered one although small oxido-reduction peaks of the polymer remain. The ion exchange could not be restored even by retreatment with NO_3^-. In the case of vitreous carbon, the redox peaks in 0.01 M NaOH are obtained at potentials more negative than those occurring in 0.1 M NO_3^-, pH 12. It was postulated that the incorporation of OH^- is enhanced under these experimental conditions. Then, the transport of OH^- through the PPy film results in considerable changes when passing from vitreous carbon to Al. In the case of Al the transport of OH^- in the polymer is followed by oxidation of the substrate. The oxidation products gradually undermining the polymer film.

Fig. 5a shows the electrochemical response obtained in 0.1 M $CH_3CO_2^-$, pH 12. A similar result was obtained upon replacing $CH_3CO_2^-$ by $C_2O_4^{2-}$ (Fig. 5b). Electrodeposition of PPy on vitreous carbon could not be performed in alkaline solutions containing these anions due to their basic character [11]. Moreover, these anions cannot re-intercalate to replace the expelled NO_3^- and as a result, the OH^- is incorporated into the polymer film. The comparison between the voltammetric response obtained in Fig. 5 to that obtained with PPy-coated vitreous carbon electrode in 0.01 M NaOH [11], suggests that OH^- is also incorporated into the polymer film in the case of Al. On the other hand, the cyclic voltammograms in the presence of $CH_3CO_2^-$ or $C_2O_4^{2-}$ appear to be more stable and with well-defined peaks when they are compared with the response obtained for PPy-coated Al electrode in 0.01 M NaOH (Fig. 4). This effect is probably associated with the fact that these anions play a role in the Al electrode passivation. It is known that $CH_3CO_2^-$ and $C_2O_4^{2-}$ inhibit

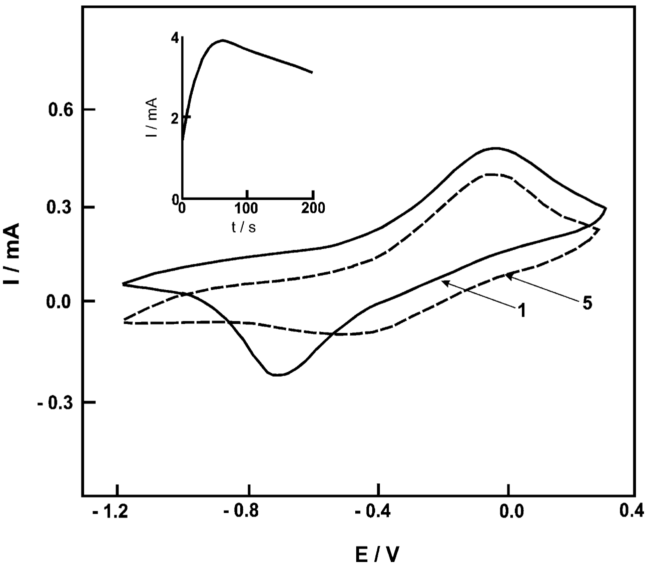

Fig. 6. Cyclic voltammograms of PPy-coated Al electrode in 0.1 M $\mathrm{SO_4}^{2-}$, pH 12 solution at 0.05 V s^{-1}. The film was made potentiostatically (E = 0.90 V, t = 30 s) in $\mathrm{SO_4}^{2-}$, pH 12 solution containing 0.5 M Py. The cycle numbers are indicated. The I/t curve for 200 s is also included.

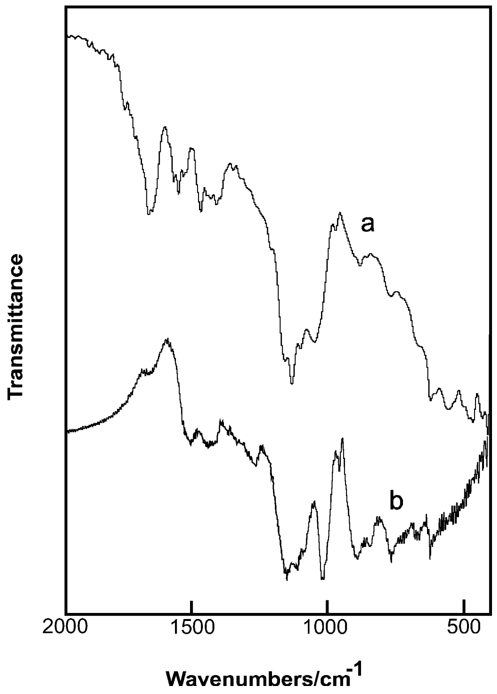

Fig. 7. Infrared spectra of (a) PPy deposited on Al at 0.90 V in 0.1 M $\mathrm{SO_4}^{2-}$, pH 12 solution containing 0.5 M Py; (b) the film after the potentiodynamic polarisation shown in Fig. 6.

the pitting corrosion of Al and Al alloys in neutral media [13–15].

The electrosynthesis of homogeneous and adherent PPy film on Al can also be performed in 0.1 M $\mathrm{SO_4}^{2-}$, pH 12 solution containing Py at a constant applied potential. Fig. 6 shows the current-time response during the potentiostatic polarisation. As in the case of $\mathrm{NO_3}^{-}$, the formation of a passive oxide layer occurs first, followed by the nucleation and growth of the polymer. The IR spectrum of the film is shown in Fig. 7a. The absorption bands at 1125 and 1045 cm^{-1} are attributed to stretching modes of distorted $\mathrm{SO_4}^{2-}$ anions, $\nu_3(\mathrm{SO_4}^{2-})$ [12], indicating the incorporation of these anions as dopants in the polymer film. The peaks in the range from 1580 to 1390 cm^{-1} are due to C=C and C=N in plane vibrations. The IR spectrum of the film cycled in the solution without the monomer shows that the absorption bands characteristic of $\mathrm{SO_4}^{2-}$ almost disappear (Fig. 7b). The bands at 1163 and 1025 cm^{-1}, associated with C–H bonds deformations, and the shoulder at 1123 cm^{-1}, assigned to the breathing vibration of the pyrrole ring, can now be seen due to the disappearance of the $\mathrm{SO_4}^{2-}$ bands.

The doping/undoping curve of the $\mathrm{SO_4}^{2-}$-formed film in a solution without the monomer is presented in Fig. 6. The stabilised voltammogram exhibit oxidation and reduction peaks at 0.06 and −0.72 V, respectively. A noticeable feature in the curves is that the redox peaks appear again superimposed on a large anodic current in the first cycle. This large background current decreases during the subsequent scans until reaching a stabilised value. It is also possible to form PPy films by repeated potential linear scanning in $\mathrm{SO_4}^{2-}$ solution. The voltammetric curve is characterised by a rapid growth of the Py oxidation wave starting at about 0.65 V and by anodic and cathodic waves associated with the polymer film (Fig. 8, small insert). As with $\mathrm{NO_3}^{-}$ [8], the potentiodynamic technique does not lead to the formation of very stable films. The cyclic voltammograms of the PPy-covered electrode also shows large background anodic currents in the potential region where the film is oxidised and reduced (Fig. 8). As in the case of $\mathrm{NO_3}^{-}$, the galvanostatic mode was found to be unfavourable for PPy deposition onto Al.

One can suppose that an incomplete coverage of the electrode by the polymer results in an enhanced oxidation of

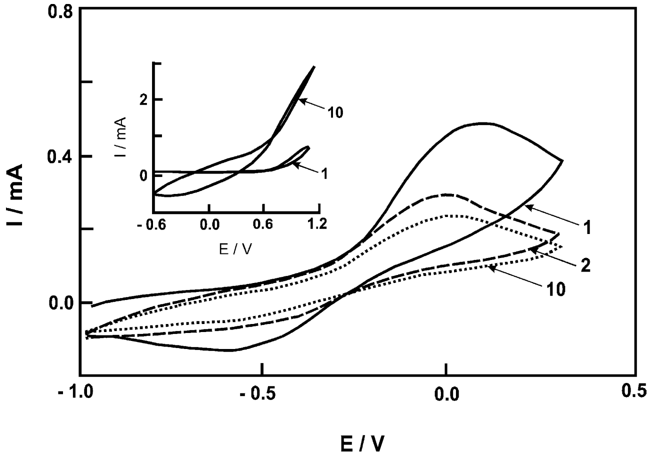

Fig. 8. Cyclic voltammograms of PPy-coated Al electrode in 0.1 M $\mathrm{SO_4}^{2-}$, pH 12 solution at 0.05 V s^{-1}. The cycle numbers are indicated. The film was made potentiodynamically at 0.05 V s^{-1} in $\mathrm{SO_4}^{2-}$, pH 12 solution containing 0.5 M Py (small insert).

the Al substrate and that the anodic current measured during the PPy cycling is associated with this process. If this explanation were correct, a different response should be seen with a PPy film formed in NO_3^- and cycled in SO_4^{2-} solution. However, the cycling behaviour in SO_4^{2-} of a film formed in NO_3^- also presents a high anodic background current, unlike the behaviour of the same film in NO_3^-, which does not present this current. Thus, the effect is not due to the presence of uncovered areas of the substrate exposed to the solution. A previous work has shown that the redox behaviour of PPy formed on a vitreous carbon electrode in SO_4^{2-} is not the same as that obtained in NO_3^- [11]. During the first reduction, SO_4^{2-} is released, but these anions are not incorporated into the polymer matrix when the potential is reversed, in agreement with the IR results (Fig. 7b). It has been postulated that the transport of OH^- was the most important process to maintain the film electroneutrality and that the substitution of the SO_4^{2-} anions by the OH^- anions resulted in a decrease of redox activity compared to that obtained with anions like NO_3^-. The present results also provide evidence to suggest that in the case of Al, the penetration of the PPy film by OH^- is followed by oxidation of the substrate, so that that the current associated with this dissolution is observed simultaneously with the redox response of the polymer. Thus, in spite of the fact that SO_4^{2-} is a suitable electrolyte for PPy electrodeposition on Al, it is less favourable for cycling the polymer than NO_3^-. The film presents very good redox properties in NO_3^- when lower oxidation currents of the metal base are observed. It is interesting to mention that when PPy films synthesised in SO_4^{2-} are cycled in NO_3^-, the behaviour of the film turns to that obtained in NO_3^- after a few repetitive voltammetric cycles.

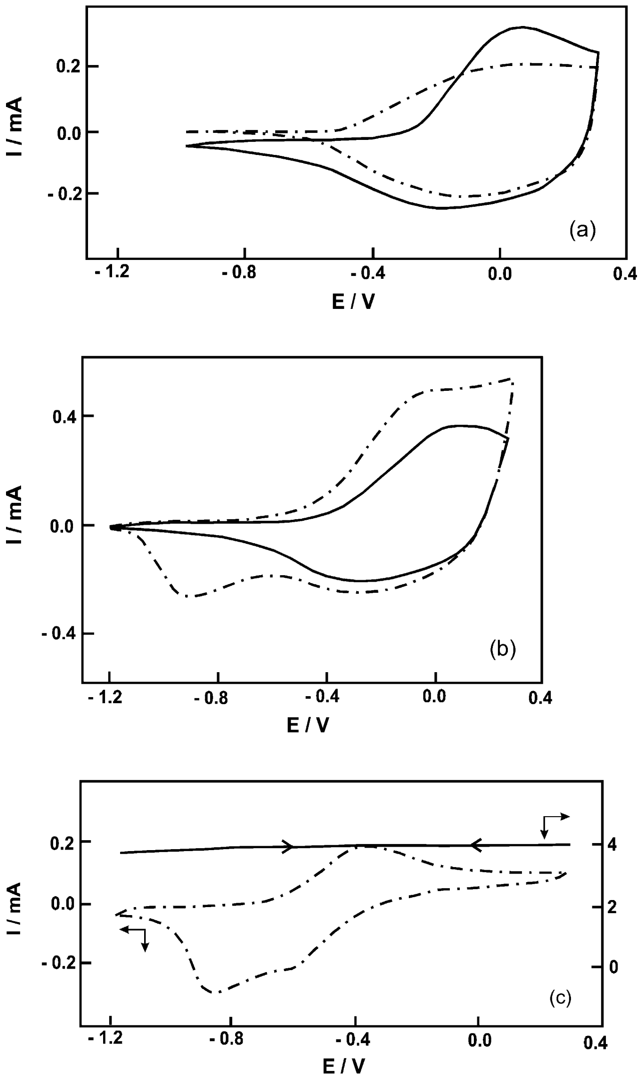

Fig. 9. Effect of pH on the potentiodynamic polarisation of PPy-coated Al (full line) and PPy-coated vitreous carbon electrode (discontinuous line) at $0.05\,V\,s^{-1}$ in (a) 0.1 M HNO_3; (b) 0.1 M NO_3^-, pH 7 and (c) 0.1 M NO_3^-, pH 13. The film was formed potentiostatically at 0.90 V in 0.1 M NO_3^-, pH 12 solution containing 0.5 M Py.

3.2. *Effects of pH*

The influence of pH on the redox response of PPy films synthesised in 0.1 M NO_3^-, pH 12 solution was analysed. The curves obtained under the same experimental conditions for films formed on vitreous carbon [11] are superimposed to compare. Fig. 9a shows that the electrochemical response obtained in 0.1 HNO_3 for PPy films formed on Al and on vitreous carbon are not very different. Thus, the charge compensation is made mainly by the transport of NO_3^- in both substrates. Only the first cycle is displayed due to the properties of the film formed onto Al change during cycling, as it will be shown in the next section. Likewise, the voltammetric curve of the PPy-coated Al electrode is very similar to that obtained for the film formed in acid media [7]. The film formed onto Al is very stable (if it is not submitted to very negative potentials) because NO_3^- inhibits Al dissolution [16].

The redox voltammogram in neutral and weakly acid media of PPy synthesised on Al is similar to that obtained at pH 12, as already observed on vitreous carbon (Fig. 9b). The film can be doped and undoped without loosing its redox behaviour because the stability of the oxide film at this pH values.

The cycling of PPy formed on Al differs markedly from that synthesised on vitreous carbon when a strong alkaline solution is employed (Fig. 9c). PPy switching is not hindered in strong alkaline solution when the substrate is vitreous carbon. It was found that under these experimental conditions the incorporation of OH^- is enhanced, while the incorporation of NO_3^- is suppressed. The redox ability of the PPy disappears at pH 13 when the film is formed on Al. Immediately after immersing the PPy-covered Al electrode in solution of pH 13, a high oxidation current is measured as it occurred with the substrate when no PPy film was deposited. Thus, the oxidation of the substrate is the main reaction at the electrode surface.

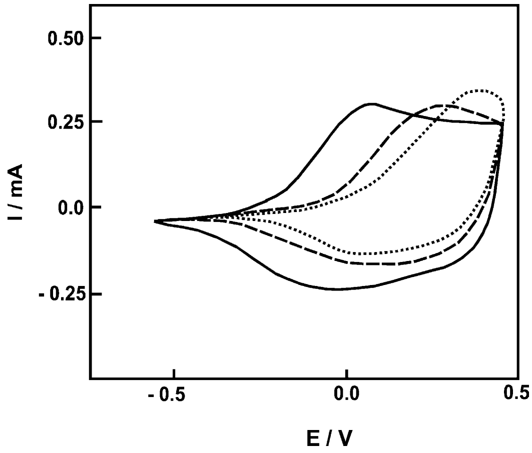

Fig. 10. Potentiodynamic polarisations of PPy-coated Al electrode in 0.1 M HNO_3 at 0.05 V s^{-1} obtained after a potential holding at −0.6 V for 0 min (—); 5 min (- - -) and 10 min (· · ·). The film was formed potentiostatically at 0.90 V in 0.1 M NO_3^-, pH 12 solution containing 0.5 M Py.

3.3. *Effects of the cathodic switching potential*

An important additional information was provided by voltammetric studies of the film with different cathodic limits of the potential variation. PPy films formed on vitreous carbon in acid or alkaline solutions were stable to cycling in acid solutions even when the negative limit was fixed at −1.5 V. On the contrary, the electrochemical behaviour of PPy formed on Al in alkaline or in acid solution significantly changed when the film is cycled in 0.1 M HNO_3. As was shown previously, the film was stable to cycling between −0.6 and 0.4 V [7]. But after holding the potential at −0.6 V for 5 min, the subsequent anodic scan shows a positive shift in the anodic peak, whereas the cathodic peak remains practically unchanged (Fig. 10). For a potential holding time of 10 min the effect is more pronounced. Maintaining a potential of −0.3 V causes only a slight potential shift. Thus, for a constant potential holding time, the effect becomes more pronounced as the holding potential is more negative. By extending the negative limit to −1.0 V, the shift in the anodic peak occurs during cycling without a potential holding (Fig. 11). Successive scans resulted in a gradual decrease of the film redox currents due to an incomplete oxidation of the film. The electrochemical activity cannot be restored by changing the negative potential limit to more positive values or by cycling the covered electrode in a less acidic solution. The same behaviour was also found when PPy was cycled in 0.1 M H_2SO_4, indicating that the decrease in the film activity is not affected by the nature of the anion. On the other hand, the stability of the film on inert electrodes under the same experimental conditions suggests that the effect is not due to decomposition of the film itself. The irreversible loss of activity when the film formed on Al is submitted to very negative potentials in acid solution might be explained in terms of the H^+ reduction to H_2. The fact that proton reduction occurs is an evidence of the penetration of the film by the electrolyte followed by redox reactions at the substrate. The recombination of H^+ results in a much lower concentration of these ions, causing a local pH increase at the Al surface. As a result of this process, a more stable and less soluble oxide film begins to form. This oxide is sufficiently protective to inhibit the oxidation and reduction processes of the polymer. Another explanation may be that the polymer film formed onto Al becomes more compact than the film deposited on vitreous carbon when it is subjected to negative potentials. As a result an additional overpotential is required for their oxidation.

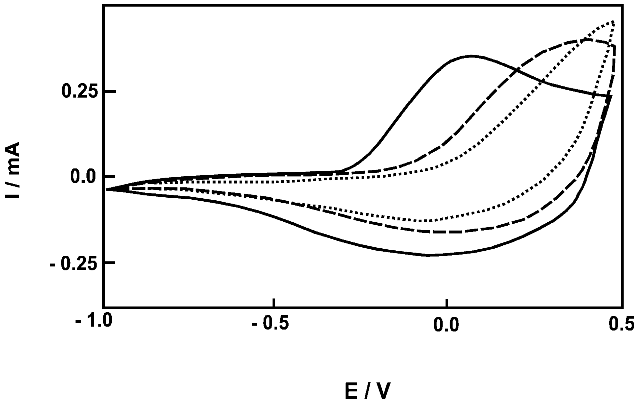

Fig. 11. Cyclic voltammograms of PPy-coated Al electrode in 0.1 M HNO_3 at 0.05 V s^{-1}. The film was formed potentiostatically at 0.90 V in 0.1 M NO_3^-, pH 12 solution containing 0.5 M Py. Scans 1 (—), 2 (- - -) and 3 (· · ·) are displayed.

4. Conclusions

Among the various alkaline electrolytes used, NO_3^- was found to be the only anion able to give a low dissolution of the Al electrode, allowing cycling of the polymer film. The PPy film generated is less porous than that formed in acid media. The difference between the redox behaviour in NO_3^- and that obtained in the presence of the other anions analysed lies in the type of ion transport. While the transport of NO_3^- is dominant, in the presence of the other anions the exchange of OH^- occurs. The increase in the contribution of OH^- to the ion transport is responsible of enhanced Al dissolution and the loss of PPy activity. In spite of the fact that well-adherent PPy deposits are formed in SO_4^{2-} solution, this anion is replaced by OH^- during the oxidation/reduction of the film.

Aluminium ions generated by the electrochemical oxidation probably contribute to the ion exchange process in the polymer.

Acknowledgements

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References

[1] G. Inzelt, M. Piner, J.W. Schultze, M.A. Vorotyntsev, Electrochim. Acta 45 (2000) 2403.
[2] K.M. Cheung, D. Bloor, G.C. Stevens, Polymer 29 (1988) 1709.
[3] F. Beck, P. Hülser, J. Electroanal. Chem. 280 (1990) 159.
[4] P. Hülser, F. Beck, J. Appl. Electrochem. 20 (1990) 596.
[5] K. Naoi, M. Takeda, H. Kanno, M. Sakakura, A. Shimada, Electrochim. Acta 45 (2000) 3413.
[6] G. Smitha Akundy, J.O. Iroh, Polymer 42 (2001) 9665.
[7] S.B. Saidman, J.B. Bessone, J. Electroanal. Chem. 521 (2002) 87.
[8] S.B. Saidman, J. Electroanal. Chem. 534 (2002) 39.
[9] D.E. Tallman, C. Vang, G.G. Wallace, G.P. Bierwagen, J. Electrochem. Soc. 149 (2002) C173–C179.
[10] D.E. Tallman, C. Vang, M.P. Dewald, G.G. Wallace, G.P. Bierwagen, Synth. Met. 135/136 (2003) 33.
[11] S.B. Saidman, Electrochim. Acta 48 (2003) 1719.
[12] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, third ed., Wiley, New York, 1978.
[13] G. Lyberatos, L. Kobotiatis, Corrosion 47 (1991) 820.
[14] K.N. Kobotiatis, N. Kioupis, P.G. Koutsoukos, Corrosion 53 (1997) 562.
[15] Z. Szklarska-Smialowska, Pitting Corrosion of Metals, National Association of Corrosion Engineers, Houston, TX, 1986.
[16] D.D.N. Singh, R.S. Chaudhary, C.V. Agarwal, J. Electrochem. Soc. 129 (1982) 1869.