PREPARATION OF POLYPYRROLE BY DIRECT ELECTROCHEMICAL OXIDATION OF PYRROLE ON PARAFFIN IMPREGNATED GRAPHITE ELECTRODE

Mária FILKUSOVÁ[a,*], Renáta ORIŇÁKOVÁ[b1], Kvetoslava MARKUŠOVÁ[b2] and Karol KOVAĽ[c]

[a] *Department of Physical Chemistry, Faculty of Science, Comenius University, Mlynská dolina, SK-842 15 Bratislava 4, Slovakia; e-mail: maria.filkusova@gmail.com*
[b] *Institute of Chemistry, Faculty of Science, P. J. Šafárik University, Moyzesova 11, SK-04154 Košice, Slovakia; e-mail: [1] renata.orinakova@upjs.sk, [2] kveta.markus@gmail.com*
[c] *Institute of Material Research, Slovak Academy of Science, Watsonova 47, SK-04353 Košice, Slovakia; e-mail: kkoval@imr.saske.sk*

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The formation of polypyrrole (PPy) layers by electrochemical polymerisation of pyrrole (Py) on paraffin impregnated graphite electrode (PIGE) was studied. Electrochemical oxidation of Py was studied by means of cyclic voltammetry (CV) and the morphology of the deposited layers was investigated with scanning electron microscope (SEM). The structure and quality of PPy layers on PIGE depends on monomer concentration, pH value, stirring intensity and scan rate during the polymerisation process.

Keywords: Pyrrole; Polypyrrole; Electrochemical polymerisation; Paraffin impregnated graphite electrode.

Conducting polymers (CPs) represent a class of versatile synthetic materials with both attractive mechanical properties and advantages of polymer processing[1–3]. They comprise the wide range from insulators to metals.

Synthesis of CPs can be accomplished chemically or electrochemically. By the chemical method, monomers are oxidized by oxidizing agents or catalysts. On the other hand, the electrochemical polymerisation involves the direct formation of CPs with better control of film thickness and morphology, which makes them suitable for use in electronic devices[4–7]. Owing to combination of unique mechanical, electrical, optical and membrane properties, these polymers are promising for diverse applications including antistatic coatings, batteries, supercapacitors, electrochromic devices and electroluminescent displays, LEDs, corrosion protection, analytical chemistry etc.[1,4,8–10]

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Polypyrrole (PPy) is a frequently studied and used material from the group of polymers with heteroatoms. The wide interest in the study of the properties of PPy has been manifested by the large amount of published work during the past decade[11]. The water-soluble, commercially available pyrrole monomer (Py) is easily oxidized in a wide pH range and retains good redox properties. Polypyrrole exhibits good electrical conductivity, is relatively stable under ambient conditions and is easy to synthesize both chemically and electrochemically[4,5,7,12]. In both cases, it is obtained in an oxidized (doped), high conductivity state[13]. Polypyrrole is one of the most promising conducting polymers used in sensor design because of its convenient deposition from aqueous solutions, high conductivity and relative stability in its oxidized doped state as long as over-oxidation is avoided[14]. The properties mentioned predestined PPy for use in biosensors, gas sensors, microactuators, antielectrostatic coatings, solid electrolytic capacitors, electrochromic windows and displays, polymeric batteries, electronic devices, functional membranes, etc.[6]. Polypyrrole is a very attractive polymer for corrosion protection applications. An important and particularly promising area of its application are electrochemical sensors: potentiometric, voltammetric/amperometric and those using resistance changes measurements[8,15–17].

Polypyrrole layers with different characteristics are obtained through varying the preparation conditions. The effect of pH on the electrochemical polymerisation of Py onto Al electrodes in nitrate solution was investigated by Saidman[15]. The solution with pH 12 was the only one that allowed electropolymerisation. The influence of Al oxide characteristics and nitrate concentration on the electropolymerisation process was discussed.

The effect of preparation temperature on the conductivity of PPy conducting polymer prepared by an electrochemical method in an aqueous medium using camphor sulphonate has been reported by Kassim et al.[4]. The conductivity decreases with increase in temperature and the optimum temperature was found between 10 and 30 °C. The results show that the polymer produced at low temperature has higher conductivity and is stronger than that originated at higher temperatures.

The chemical reactivity of PPy and the influence of different chemical processes on changes of the polymer structure, composition as well as on possible degradation was analysed by Maksymiuk[8]. The benefits and disadvantages of such processes for analytical characteristics of PPy based electrochemical potentiometric ion sensors were considered. It was found that the parameter, which is most seriously affected by the spontaneous processes, is the detection limit of the sensor[8].

The electrochemical polymerisation of Py on stainless steel substrates using rotating disc electrode with the aid of galvanostatic technique at different experimental conditions was studied in another paper[18]. The results obtained showed that various morphologies were obtained by changing the current density and/or disc rotation speed. Apart from conventional morphologies of PPy coatings reported in the literature, a new semicrystalline morphology was obtained under the conditions of very low current density.

The performance of polymer films depends on their nature, characteristics and morphology. These properties can be regulated by a variety of synthesis conditions including the type of counter-ion and solvent and their concentrations, current density, substrate rotation speed, pH and temperature of the solution. Moreover, it was reported that properties, such as adhesion, corrosion resistance and conductivity are also affected by the morphology of polymer layer[4,18].

In the present paper electrochemical deposition of PPy layers on a paraffin impregnated graphite electrode (PIGE) was performed using cyclic voltammetry (CV). The main argument for application of this electrode was the possibility to achieve good reproducibility of the surface in contrast to the bad reproducibility of some metallic electrode surfaces. Thus, the reproducibility of voltammetric measurements consisted especially in the relatively constant background current corresponding to almost constant electrode surface area. Further advantages of PIGE are: simple preparation, easy renewal of the surface and reasonable price[19–21]. The aim was to investigate the electropolymerisation process of Py on PIGE as a function of monomer concentration, pH value of the electrolyte, scan rate and stirring. The morphology of the resulting layers produced under various experimental conditions is reported. This study was motivated by the intended ambition to prepare the suitable template for the construction of composite metal/conducting polymer electrocatalysts for hydrogen evolution. Hence, the cathodic activity of prepared PPy layers for hydrogen evolution in acidic media was also studied.

EXPERIMENTAL

Polypyrrole films were electrochemically synthesized by multiple scan CV using a supporting electrolyte containing 0.1 M NaCl. Three Py monomer concentrations were applied: 0.006, 0.06 and 0.6 mol/l. The pH of the electrolyte solution was adjusted to 2.2, 5.6 or 11.2 by addition of HCl or NaOH. The working electrode was typically cycled for 10 cycles between –800 and +1100 mV (vs Ag|AgCl|3 M KCl), beginning at –800 mV, with scan rate 25 or 50 mV/s in order to affect electropolymerisation. The electrolyte solution was degassed by nitrogen purging. All chemicals were of analytical grade and solutions were freshly prepared with distilled water. Py monomer (Pyrrole, 98+%) was purchased from Sigma–Aldrich and used as received.

The electrocatalytic activity of PPy layers in the hydrogen evolution reaction was studied between –200 and –1200 mV (vs Ag|AgCl|3 M KCl) in 0.1 M H_2SO_4 solution at a scan rate 1 mV/s at room temperature.

All CV experiments were carried out with an EcaStat potentiostat/galvanostat, model 110 V (Istran, Slovakia). The electrochemical cell consisted in a classical three-electrode set-up with an Ag|AgCl|3 M KCl electrode as a reference electrode, a large-area platinum electrode as a counter electrode and a graphite/paraffin composite rod with a 6 mm diameter as a working electrode. The surface area of CE was 5.4 cm^2.

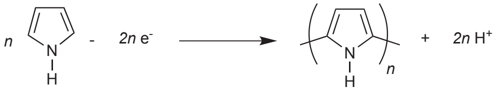
To obtain reproducible results, the surface of PIGE was mechanically renewed with emery paper, polished on glossy paper, then washed with distilled water and degreased with acetone. The platinum electrode was cleaned in nitric acid (1:1) and rinsed with distilled water before use.

Morphology of synthesized PPy films was characterised ex situ using a TESLA BS 340 scanning electron microscope (SEM). The operating voltage for the SEM was maintained at 20 kV throughout the analysis.

RESULTS AND DISCUSSION

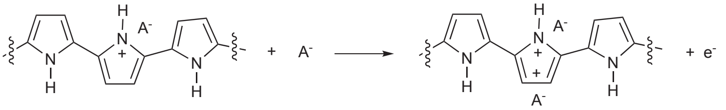
Electrochemical Polymerisation of Pyrrole

In an electrochemical polymerisation of Py, the monomer is oxidized at the surface of the positively polarized working electrode. As a result of the initial oxidation, the radical cation of the monomer is formed and reacts with other monomers present in solution to form oligomeric products and then the polymer. The resulting reaction can be expressed in the aqueous solution by the following reaction[1].



(*1*)

The electropolymerisation gives the oxidised conducting (doped) PPy. The final polymer chain carries a positive charge every 3 to 4 Py units, which is counter-balanced by an anion (A$^-$) [22]. At more positive potentials, PPy undergoes overoxidation, which has often been regarded as an undesirable degradation process[5,23,24].



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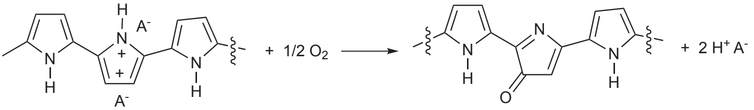

(*2b*)

The overoxidative degradation is mainly characterised by splitting of conjugated double bonds and macromolecular crosslinking and/or by the attack of nucleophiles from the solution on the charged polymeric lattice. According to Trueba et al.[25], the dominating factor of this process is the solution composition. In weakly nucleophilic media the crosslinking mechanism will prevail over the nucleophilic one. With the increase of medium nucleophilicity, the contribution of the latter, and thus, the degree of the polymer functionalization rises[25,26]. In aqueous solution, the PPy overoxidation potential depends on the solution pH – the higher the pH the lower the overoxidation potential. The irreversible overoxidation occurred much more easily in an alkali solution. It has been proposed by some researchers that the PPy overoxidation is due to water oxidation[13,27].

Evolution of molecular oxygen also can proceed on the working electrode at potentials higher than the decomposition potential of acidic water (1.23 V vs SCE) according to the following reaction.

$$2\ (H^+OH^-) \rightarrow O_2 \uparrow + 4\ H^+ + 4\ e^- \qquad (3)$$

In chloride-containing aqueous solutions, another oxidation process occurring on the electrode surface at higher anodic potentials is the chlorine evolution reaction.

$$2Cl^- \rightarrow Cl_2 \uparrow + 2\ e^- \qquad (4)$$

The value of the equilibrium potential of chlorine evolution is more positive (1.33 V vs SCE) than that of oxygen evolution, consequently, the oxygen evolution should be preferred. Local acidification near the anode layer and other kinetic conditions may lead to the predominance of the chlorine evolution reaction[28].

The hydrogen gas releases at the counter electrode during the electropolymerisation process.

$$2n\ H^+ + 2n\ e^- \rightarrow n\ H_2 \uparrow \tag{5}$$

Cyclic Voltammograms

Cyclic voltammetry is an essential method for the characterization of the electrochemical properties of CPs. Although the shape of cyclic voltammograms has been for long a subject of discussion, it is now accepted that the shape and position of cyclic voltammograms can reflect the properties of polymer structure[29].

Polypyrrole films were synthesized onto graphite electrode by means of CV method in solutions composed of Py monomer and NaCl. The polymerisation was continued for 10 cycles.

The voltammetric curves obtained in supporting electrolyte (SE) in the absence of Py provide information about the characteristics of the working electrode surface. As may be seen in the Fig. 1a, the voltammetric curve of SE exhibits almost constant currents in the whole range of potentials. On the other hand, cyclic voltammograms registered in presence of Py in the same SE show in the first anodic scan an exponential current increase starting at about 0.6 V (Fig. 1b). A characteristic feature of the first potential cycle is the nucleation loop. Such behaviour appears when a freshly polished electrode is used and the scan is reversed at a potential close to the peak potential. It is similar in respect to the electrochemical deposition of metal on a foreign substrate, in which an overpotential is required for nucleation and then further growth of the metallic layer occurs at the characteristic redox potential of the metal, leading to a trace-crossing on the reverse sweep[30].

Let us mark the anodic current appearing in the first scan as i_{MOx}, for it is associated with irreversible oxidation of the pyrrole monomer to produce the Py radical cation. From the second scan on a new anodic current (let us mark it i_{POx}, for it is consistent with the reversible oxidation of the electrosynthetized PPy polymer) appears at gradually less positive potentials (Fig. 1a). On reverse scans a cathodic wave i_{PRed} (corresponding to reduction of the oxidized polymer) was registered (Fig. 1) as a counterpart to the reversible anodic current i_{POx}. The magnitude of the PPy redox currents increased and shifted to more positive potentials with the voltammetric cycle number indicating the build-up of electroactive PPy film on PIGE with each cycle (Fig 1a).

Representative data for the electropolymerisation of Py from the solutions containing 0.006, 0.06 and 0.6 M Py for different pH values are shown in Figs 2, 3 and 4, respectively, at potential scan rate 25 mV/s (Figs 2–4a, 2–4b) and 50 mV/s (Figs 2–4c, 2–4d) without stirring of electrolyte solution

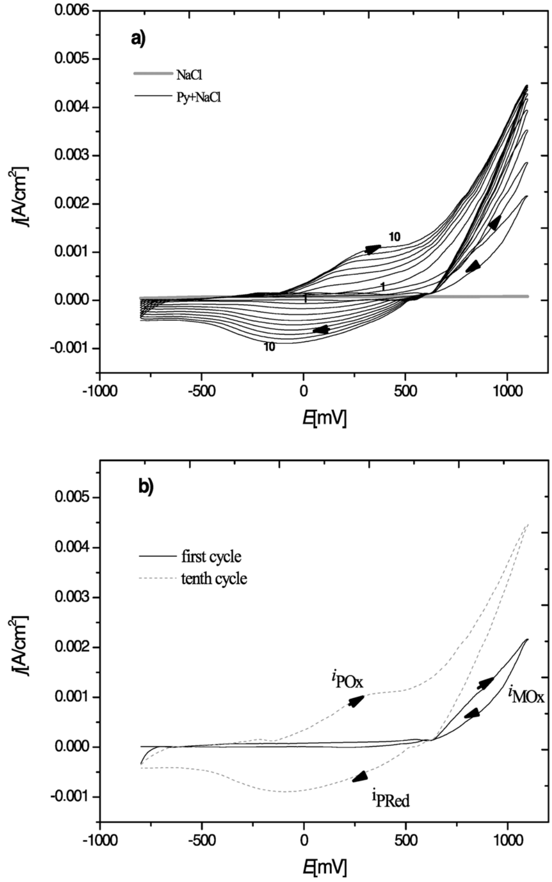

FIG. 1

Voltammetric curves obtained between –800 and +1100 mV (vs Ag|AgCl|3 M KCl) in 0.1 M NaCl supporting electrolyte alone and supporting electrolyte containing 0.06 M Py on PIGE at 25 mV/s, pH 2.2, without stirring for 10 cycles (a). The first and tenth cycles of electropolymerisation of pyrrole are shown (b)

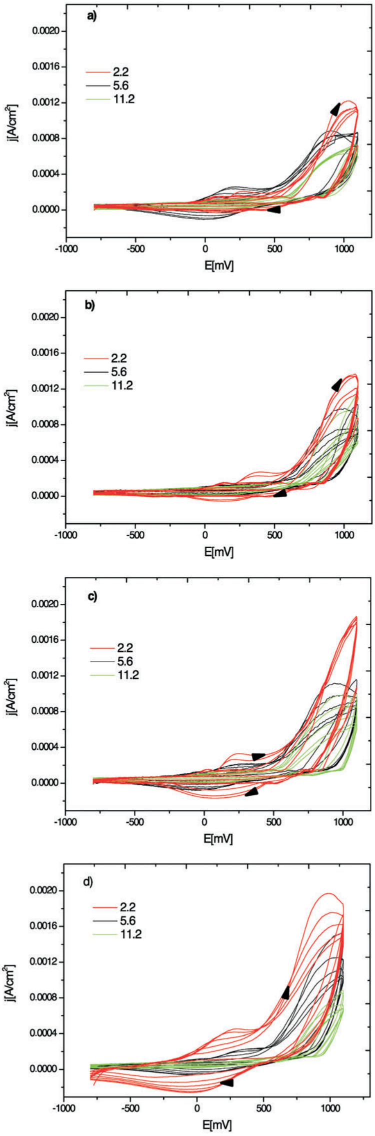

FIG. 2
Electropolymerisation of pyrrole on PIGE between –800 and +1100 mV (vs Ag|AgCl|3 M KCl) from the solution containing 0.006 M Py for different pH: at potential scan rate 25 mV/s, without stirring of electrolyte solution (a); at potential scan rate 25 mV/s, with rate of stirring 230 rpm (b); at potential scan rate 50 mV/s, without stirring of electrolyte solution (c); at potential scan rate 50 mV/s, with rate of stirring 230 rpm (d)

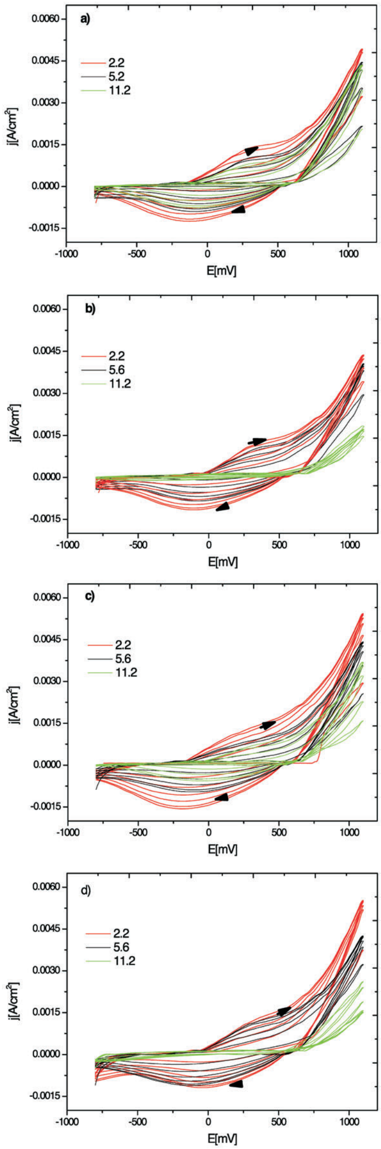

FIG. 3
Electropolymerisation of pyrrole on PIGE between –800 and +1100 mV (vs Ag|AgCl|3 M KCl) from the solution containing 0.06 M Py for different pH: at potential scan rate 25 mV/s, without stirring of electrolyte solution (a); at potential scan rate 25 mV/s, with rate of stirring 230 rpm (b); at potential scan rate 50 mV/s, without stirring of electrolyte solution (c); at potential scan rate 50 mV/s, with rate of stirring 230 rpm (d)

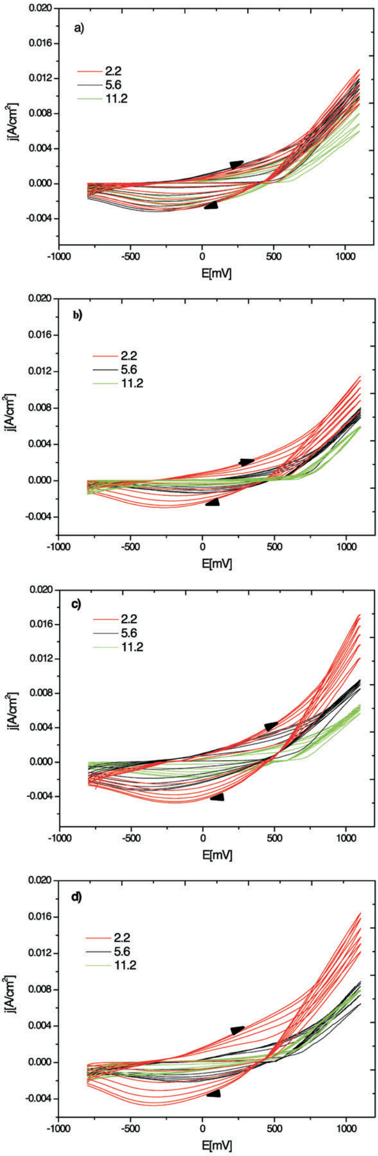

FIG. 4
Electropolymerisation of pyrrole on PIGE between –800 and +1100 mV (vs Ag|AgCl|3 M KCl) from the solution containing 0.6 M Py for different pH: at potential scan rate 25 mV/s, without stirring of electrolyte solution (a); at potential scan rate 25 mV/s, with rate of stirring 230 rpm (b); at potential scan rate 50 mV/s, without stirring of electrolyte solution (c); at potential scan rate 50 mV/s, with rate of stirring 230 rpm (d)

(Figs 2–4a, 2–4c) and with rate of stirring 230 rpm (Figs 2–4b, 2–4d). The potential values of the polymer redox peaks are summarised in Table I.

Generally, the highest currents were observed for highest Py concentration (0.6 mol/l) and lowest pH (2.2). The overlapping of both oxidation processes in one broad anodic wave was observed for the highest Py concentration (Fig. 4). On the contrary, for the lowest Py concentration (0.006 mol/l) the anodic voltammetric responses i_{POx} and i_{MOx} are distinctly separated for all pH values. (In addition, in pH 2.2, both reversible (oxidation and reduction) currents i_{POx} and i_{PRed} may split into two peaks for the Py concentration 0.006 mol/l (Fig. 2).) The measured redox currents decreased markedly as the Py concentration decreases. On the other hand, an increase in pH results in a slight decrease in the current. The lowest current values were observed for highest pH (11.2) indicating that electrolymerisation is more difficult in alkaline solution. Moreover, the currents in stirred electrolyte were approximately 3 times lower and the onset of the oxidation peak was shifted to less negative potentials than without stirring for mentioned alkaline pH. The nucleation loop on the first potential cycle appeared on all voltammetric curves. For medium concentration of Py (0.06 mol/l) the trace-crossing was observed also in the second cycle at potential scan rate 25 mV/s and for the highest Py concentration (0.6 mol/l) on all consecutive cycles for both potential scan rates as well for all pH values. The irreversible oxidation current i_{MOx} increased with increasing cycle number for higher Py concentration and acidic pH, but decreased for alkaline pH. The smallest decrease was observed for highest Py concentration and with concentration decrease it becomes more pronounced. The observed difference could be associated with the charge consumed in the irreversible oxidation at different conditions. In case the potential was reversed on the beginning of the irreversible oxidation and the charge consumed in oxidation process was small, than the current increased. However, when the overoxidation was initiated at more positive potentials and charge corresponding to the irreversible oxidation was higher, decrease of current was registered. The decrease of current during the repetitive potential cycling can be explained by considering that a high content of OH^- led to films of more insulating nature.

From results obtained it was found for all Py concentrations that: (i) the potential region for the reversible oxidation of PPy shifted to more anodic potentials with increasing pH; (ii) the reduction peak for PPy increased and shifted to more negative potentials when the pH decreased, excepting the lowest concentration for which the reduction peak shifted to more negative potentials when the pH was increased, suggesting the de-insertion of

TABLE I
The potential values of the polymer redox peaks for electropolymerisation of Py from the solutions containing 0.006, 0.06 and 0.6 M Py for different pH values at potential scan rate 25 and 50 mV/s without stirring of electrolyte solution and with rate of stirring 230 rpm

pH	Potential, mV											
	0.6 M Py				0.06 M Py				0.006 M Py			
	Oxid. onset	Anod. peak	Reduc. onset	Cathod. peak	Oxid. onset	Anod. peak	Reduc. onset	Cathod. peak	Oxid. onset	Anod. peak	Reduc. onset	Cathod. peak
	Without stirring of electrolyte											
	25 mV/s											
2.2	–190	342	405	–323	–160	326	506	–110	–145	264	293	136
5.6	–259	339	410	–150	–219	322	511	–110	–150	203	381	–10
11.2	–61	351	472	–77	–133	356	528	–103	–13	332	423	–138
	50 mV/s											
2.2	–313	344	409	–346	–224	304	409	–180	–325	224	349	94
5.6	–393	409	420	–84	–238	395	420	–106	–334	275	394	–45
11.2	–114	431	492	–351	–141	413	492	–47	–117	324	441	–56

TABLE I
(*Continued*)

pH	Potential, mV											
	0.6 M Py				0.06 M Py				0.006 M Py			
	Oxid. onset	Anod. peak	Reduc. onset	Cathod. peak	Oxid. onset	Anod. peak	Reduc. onset	Cathod. peak	Oxid. onset	Anod. peak	Reduc. onset	Cathod. peak
With stirring of electrolyte												
25 mV/s												
2.2	–376	450	384	–273	–99	396	557	–103	–37	386	557	128
5.6	–24	437	464	19	–93	393	563	–82	–31	346	638	19
11.2	214	486	523	–23	400	615	594	–76	225	456	662	96
50 mV/s												
2.2	–382	344	359	–346	–114	364	546	–28	–200	274	372	–5
5.6	–73	409	393	–84	–89	368	555	–226	–166	332	458	–62
11.2	145	431	406	351	406	613	604	–554	215	510	474	–43

OH^- [27]; (iii) without stirring of electrolyte the oxidation of PPy is initiated at most negative potentials in weakly acidic electrolyte, then in more acidic solution and at most positive potentials in alkaline bath; (iv) in stirred electrolyte the onset of PPy oxidation is shifted to more positive potentials in weakly acidic and alkaline pH and consequently the oxidation started at most negative potentials in solution of pH 2.2, then in solution of pH 5.6 and finally at most positive potentials in electrolyte of pH 11.2; (v) slightly (1.2–1.5 times) higher oxidation peak current values were generally observed at higher potential scan rate (50 mV/s in comparison with 25 mV/s).

From the CV studies it can be concluded that the low pH and high Py concentration favoured the electropolymerisation of Py on PIGE surface. High concentration of hydrogen protons is assumed to facilitate the polymerisation reaction. This assumption is supported also by the effect of stirring on the polymerisation. Stirring of the electrolyte shifted the polymerisation potential towards more positive values, so the polymerisation takes place at potentials higher than those needed in the case without stirring. Hydrogen gas evolution occurred on the working electrode surface during polymerisation. By stirring of electrolyte, removal of hydrogen gas from the surface is promoted thus the polymerisation is hindered.

The lowest peak currents associated with both the anodic and cathodic waves of the polymer at alkaline pH can be explained by considering that a high OH^- concentration hinders the electropolymerisation because of the nucleophilic attack to radical cations[23–27].

Surface Morphology of Polypyrrole Films

The properties of conducting polymers are strongly dependent on their morphology and structure. The PPy morphology depends on the preparation conditions, on counter ion, on working electrode surface and nature of solvent.

Electrooxidation of pyrrole monomer resulted in PPy deposition onto surface of PIGE. Scanning electron microscopy was used to investigate the morphology of the PPy films electrodeposited on PIGE surface. Characteristic SEM micrographs of PPy films produced by means of CV between –800 and +1100 mV (vs Ag|AgCl|3 M KCl) after 10 cycles from the solutions containing 0.006, 0.06 and 0.6 M Py for different pH values at potential scan rate 25 and 50 mV/s, without stirring of electrolyte solution are presented in Figs 5–7, respectively.

Microscopic observation of PIGE surface after PPy deposition from alkaline media at lower Py concentration (Fig. 5) shows that the PIGE surface

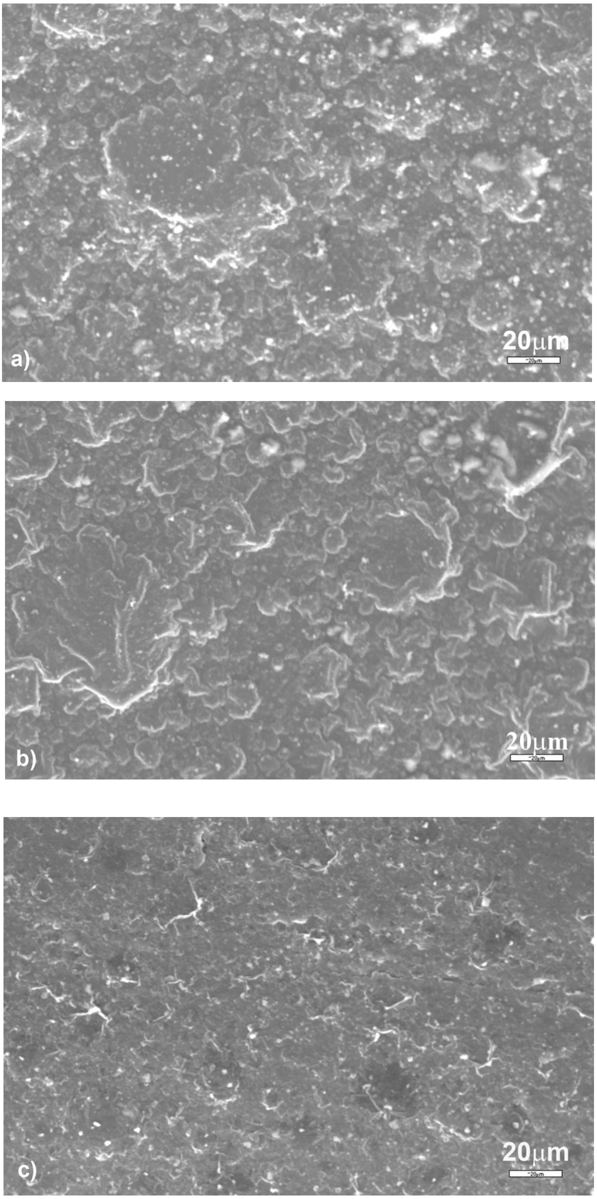

Fig. 5

SEM images of microstructures grown by CV scanning in the potential range from –1100 to +1100 mV from the solutions containing 0.006 M Py with pH 2.2 (a, c), 5.6 (b, d) and 11.2 (d, f) at potential scan rate 25 (a, b, c) and 50 mV/s (d, e, f) for 10 cycles

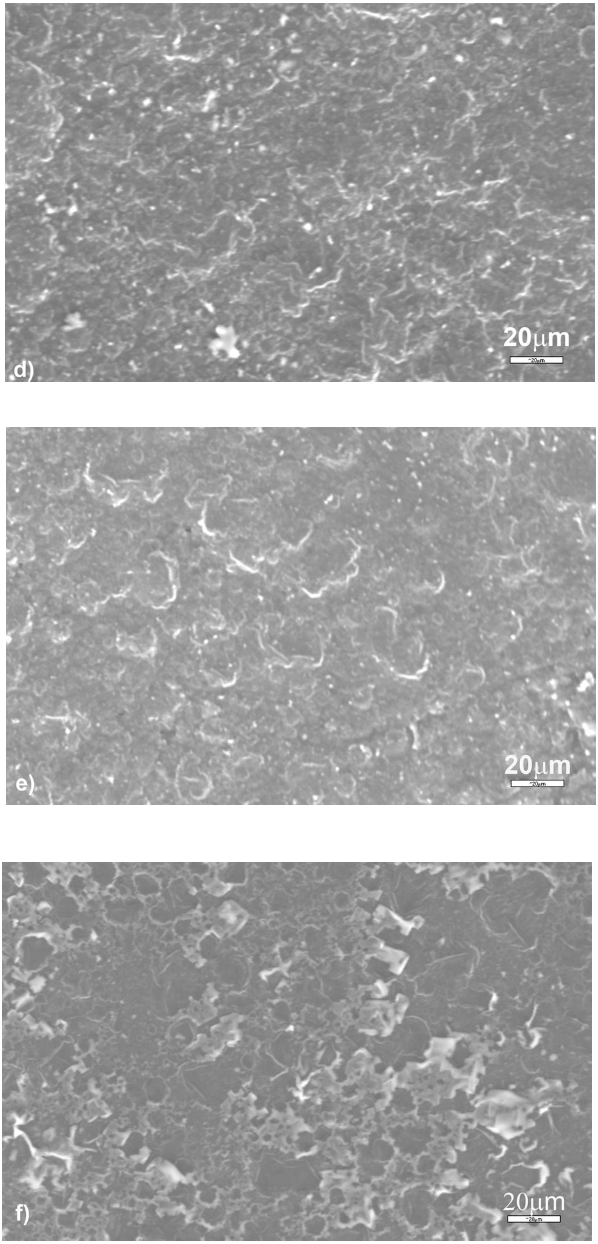

FIG. 5
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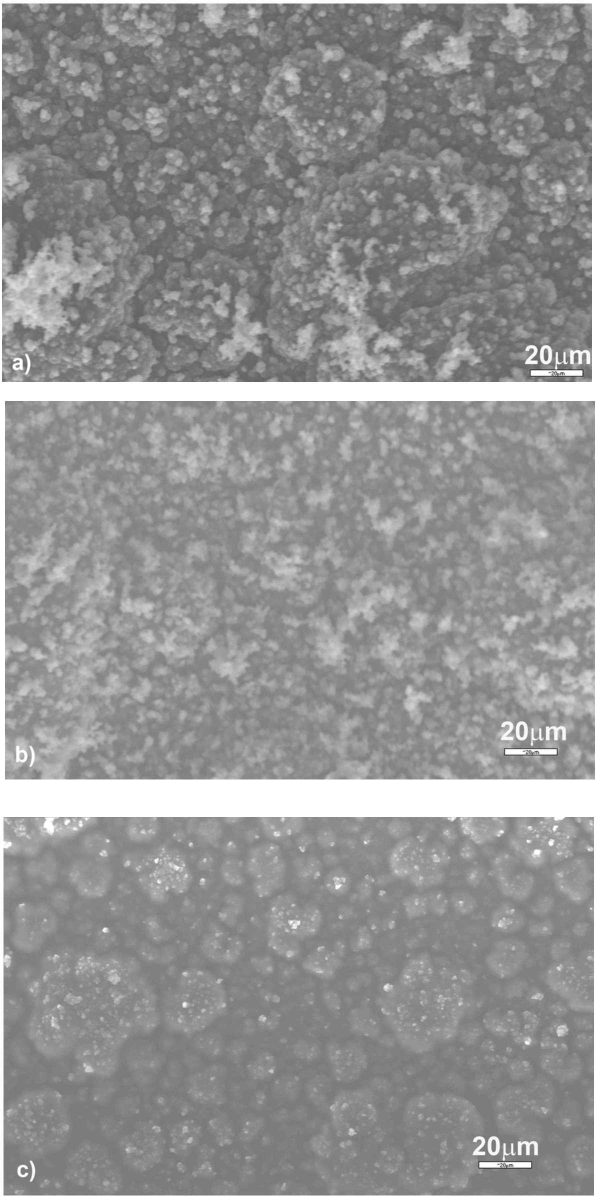

FIG. 6
SEM images of microstructures grown by CV scanning in the potential range from –1100 to +1100 mV from the solutions containing 0.06 M Py with pH 2.2 (a, c), 5.6 (b, d) and 11.2 (d, f) at potential scan rate 25 (a, b, c) and 50 mV/s (d, e, f) for 10 cycles

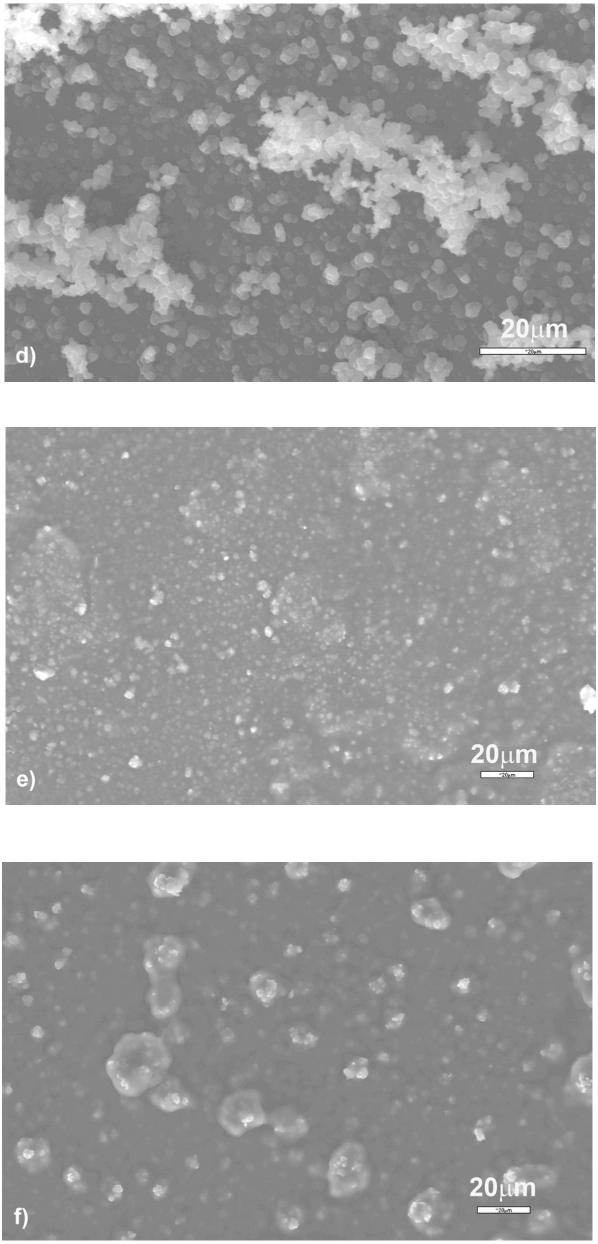

FIG. 6
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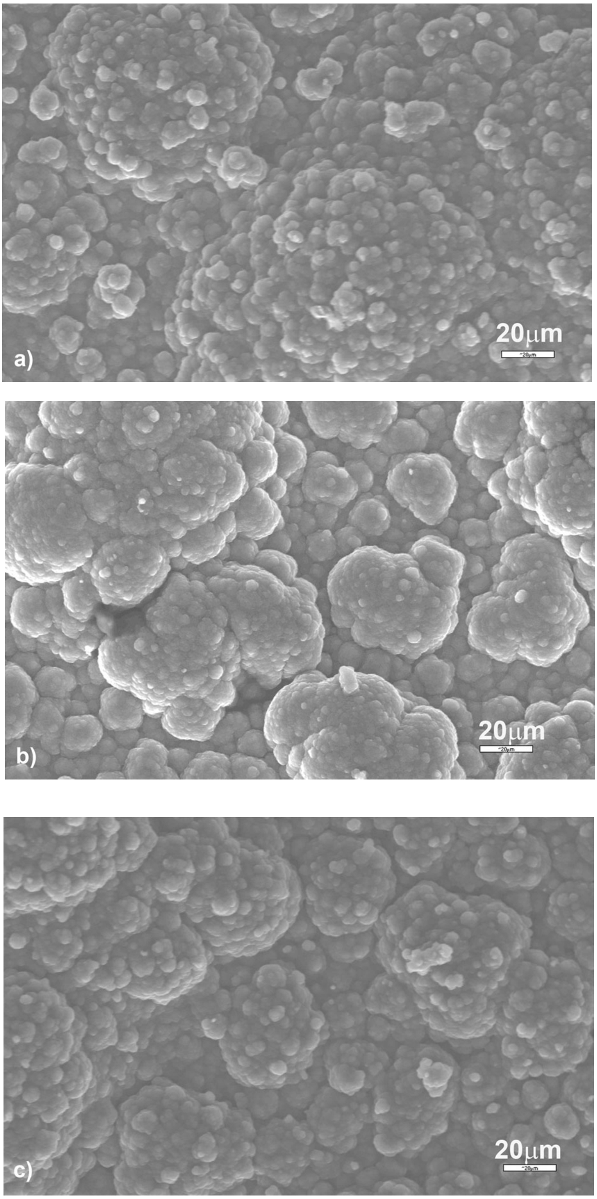

FIG. 7
SEM images of microstructures grown by CV scanning in the potential range from –1100 to +1100 mV from the solutions containing 0.6 M Py with pH 2.2 (a, c), 5.6 (b, d) and 11.2 (d, f) at potential scan rate 25 (a, b, c) and 50 mV/s (d, e, f) for 10 cycles

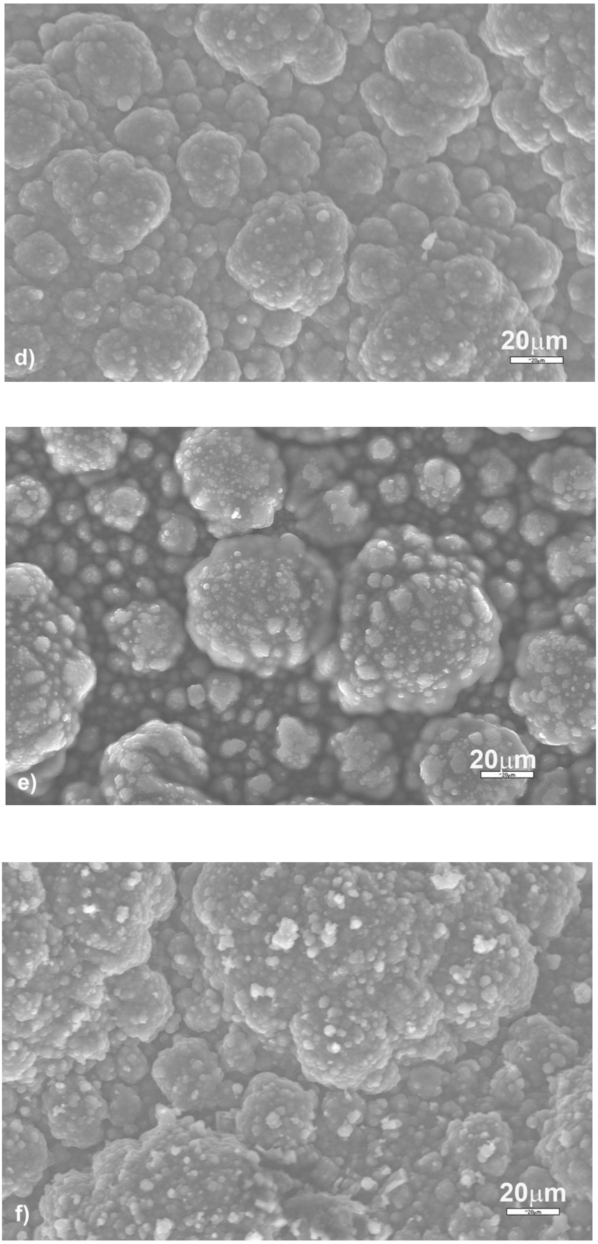

FIG. 7
(*Continued*)

was not completely covered by the polymer. Better results were obtained at higher Py concentrations (Figs 6 and 7) and for acidic pH values. In these cases, the electrode becomes rapidly covered by a black, homogeneous, thick and very adherent film. This can be explained considering that the high content of OH^- inhibits the electrochemical polymerisation of Py. Better deposition can be achieved using a higher ratio between concentrations of the Py monomer and OH^-. The same results were obtained by Lehr et al.[31].

Micrographs show the PPy films formed by overlapping globular or nodule morphology. The film is made up of many globular structures joined to one another. The nodule size increases with the concentration of Py which leads to surface roughness. Slight decrease in nodule size was observed with increase in potential scan rate as either with stirring of the electrolyte.

The surface morphology at higher potential scan rate (50 mV/s, Figs 5d–5f, 6d–6f and 7d–7f) is smoother than that at lower potential scan rate (25 mV/s, Figs 5a–5c, 6a–6c and 7a–7c). This is evident for lower concentrations of Py (Figs 5 and 6).

In acidic and weakly acidic electrolyte, the PPy films present a cauliflower-like structure constituted by micro-spherical grains. The cauliflower structure increases with an increase in Py concentration. In weakly alkaline media a semiplanar structure of coatings was observed at the lowest studied Py concentration (0.006 mol/l) (Figs 7c and 7f).

Electrocatalytic Activity

Figure 8 shows the Tafel polarization curves for HER on PPy at different pH values. The PPy layers were produced at highest Py concentration to obtain the high quality PPy film with cauliflower-like structure with large surface area. The equilibrium potential values on PPy layers for HER are shifted to less negative potentials with increasing pH. The best catalytic activity was obtained for the catalytic layer produced by polymerisation at pH 2.2. The equilibrium potential values together with Tafel slopes derived from linear plots which exhibit Tafel characteristics are listed in Table II. The lowest Tafel slopes of about –79 mV/dec were determined for PPy electrode deposited at pH 2.2. The slopes of about –94 and –124 mV/dec were obtained for PPy electrodes prepared at pH 5.6 and 11.2, respectively.

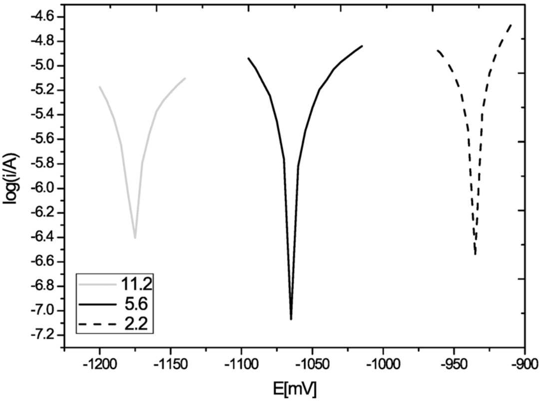

FIG. 8
Tafel polarization curves for HER on PPy electrodes in 0.1 M H_2SO_4 solution at different pH

TABLE II
Values of equilibrium potentials and Tafel slopes of the HER derived from linear plots on the PPy electrodes for different pH values

pH	E_{eq}, mV	*b*, mV/dec
2.2	–935	–79
5.6	–1065	–94
11.2	–1175	–124

CONCLUSIONS

Oxidative electrochemical polymerisation of Py from aqueous solution was studied by multiple scan CV in order to elucidate the influence of Py monomer concentration, pH value, stirring of the electrolyte solution and potential scan rate on the electrochemical polymerisation of Py on PIGE surface and on the surface appearance and quality of the electrogenerated PPy films. For the deposition of PPy on PIGE the nucleation process needs for its start an overpotential resulting in a higher current on the reverse scan at given experimental conditions.

The use of an acidic electrolyte solution for the polypyrrole synthesis on PIGE surface results in an enhanced electropolymerisation and provides a high quality PPy film with cauliflower-like structure. SEM micrographs revealed a slight decrease in nodule size with increase in potential scan rate as well as with stirring of the electrolyte. The peaks due to the oxidation and reduction of the PPy film increased intensity and shifted to more positive potentials with the voltammetric cycle number as the film growed. A decrease in Py concentration results in apparent decrease in the measured redox currents, while an increase in pH, a decrease in polarisation rate as either a stirring of the electrolyte result in a slight decrease in the current or shift in the polymerisation potential.

The PPy films deposited on PIGE from alkaline electrolyte were susceptible to the overoxidation hence the PPy reduction/oxidation and its growth were limited. High quality PPy films were obtained at highest Py concentration from acidic electrolytes on PIGE.

Microscopic observation of the PPy films synthesized from alkaline media shows that the PIGE surface was not completely covered by the polymer at lowest Py concentration. But deposition was achieved using a higher concentration of the Py monomer. Electrochemical polymerisation of Py on PIGE was affected in the main by the concentration ratio between Py monomer and H^+ or OH^- ions.

The high quality PPy films produced at pH 2.2 from the electrolyte with highest Py concentration may be used as promising matrices for development of metal/polypyrrole composite layers used as catalysts in the hydrogen evolution reaction.

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