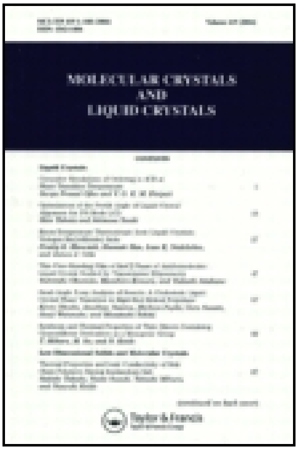

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Electropolymerization Mechanism and Electrochemical Properties of Polypyrrole Film Doped with a Large Anion

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ELECTROPOLYMERIZATION MECHANISM AND ELECTROCHEMICAL PROPERTIES OF POLYPYRROLE FILM DOPED WITH A LARGE ANION

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Using the galvanostatic method the polypyrrole films doped with common low molecular weight inorganic anions and with the large surfactant anions were obtained. The electrochemical behaviour of polypyrrole films electrosynthesised in the presence of 1,2 dihydroxybenzenedisulfonic (3,5) acid disodium salt (1,2 DHBSAS) was investigated by cyclic voltammetry. The study has been focused on the evaluation of the effects of electrosynthesis conditions on the electroresponse of the PPY films as well as on the role of the nature of the electrolyte on the doping process and on the interface properties of the polymer electrode.

The results indicate that the kinetics of the redox process are mainly governed by diffusion of the cations and anions of the supporting electrolyte (cycling electrolyte), while the large anions remain immobilized in the polymer structure. Therefore, the kinetics of the process can be monitored by changing the nature of the electrolyte and this may allow modulation of the electrical and optical properties of PPY/1,2 DHBSAS film.

Keywords: current peak; cyclic voltammogram; doped; electropolymerization; polypyrrole film; potential scan

INTRODUCTION

Among various conducting polymers, polypyrrole (PPY) films synthesized by the electrochemical oxidation of pyrrole in aqueous media are

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particularly promising on account of their unique physicochemical properties and the wide variety of their technological applications [1,2]. It is well known that the electrical and mechanical properties of PPY films strongly depend upon the synthesis conditions, for example, the type of substrate, electropolymerization potential, current density and, in particular, the nature and the concentration of the synthesis solution.

Generally, adherent PPY films are deposited on inert anodes like Pt, Au, glassy carbon or stainless steel. Several authors have reported that the synthesis of PPY in the presence of large amphiphilic surfactant anions results in the formation of films with improved mechanical and electrochemical properties [1–9]. This has been recently confirmed by showing that PPY films obtained by galvanostatic polymerization in aqueous electrolytes using the large amphiphilic SDS have high electrical conductivity [5], enhanced electroactivity [6], polystyrene – like mechanical properties [7] and sharp electrochromic contrast [8,9].

In this work we extend the study by describing the electrochemical properties of PPY films deposited from aqueous solutions containing 1,2 dihydroxybenzenedisulfonic (3,5) acid disodium salt ($C_6H_4Na_2O_8S_2$) as "doping" electrolyte. The study has been focused on the evaluation of the effects of electrosynthesis conditions (i.e. $C_6H_4Na_2O_8S_2$ concentration and current density) on the electroresponse of the PPY films as well as on the role of the nature of the electrolyte on the doping process and on the interface properties of the polymer electrode. This investigation has been carried out by cyclic voltammetry (CV).

EXPERIMENTAL

All experiments were carried out in a single-compartment electrochemical cell with the classic three electrodes configuration: a platinum wire as a working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE). A Luggin capillary tip of the reference electrode is placed as close as possible to the center of working electrode surface. This enables one to minimize ohmic drop and to use the reference electrode to detect the solution potential near the working electrode. Electrochemical synthesis is carried out using a potentiostat/galvanostat type Princeton Applied Research (PAR), Model 173 equipped with a digital coulometer. The polypyrrole films were galvanostatically deposited onto platinum substrates at $1.0\,\mathrm{mA\cdot cm^{-2}}$ and a total charge density of $360\,\mathrm{mC\cdot cm^{-2}}$. The synthesis electrolyte was a solution of pyrrole (Merck, freshly distilled, 0.05 M) and 0.05 M $C_6H_4Na_2O_8S_2$ in bidistiled water. All films showed good adherence to the platinum substrates. The electrochemical characterizations were performed using cyclic voltammetry in the –1050 mV to

+650 mV (vs. SCE) range. Before each polymerization or voltammetric study, Pt working and counter electrodes were burnt in a reduction flame. As cycling electrolyte we used a degassed 0.1 M KCl aqueous solution. All solutions were deaerated by bubbling Ar at room temperature for 20 minutes before polarization.

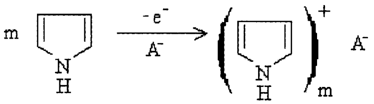
RESULTS AND DISCUSSION

Polypyrrole films were prepared galvanostatically in an aqueous solution of 0.05 M pyrrole and 0.05 M $C_6H_4Na_2O_8S_2$ (1,2 dihydroxybenzenedisulfonic (3,5) acid disodium salt) under an Ar atmosphere. Disolved oxygen was removed by bubbling the solution with argon for at least 20 minutes prior to polymerization. The thickness of the PPY film was calculated from the charge consumed with the following equation:

$$h(\mu m) = Q[M(\text{pyrrole}) + 0.22\,M(A^-)] \cdot 10^4/2.22Fd \qquad (1)$$

where Q is the charge ($C{\cdot}cm^{-2}$) consumed during electropolymerization, d is the density of a PPY(A^-) film, i.e. 1.516 $g{\cdot}cm^{-3}$ (from [1]), M molecular weight and F the Faraday constant. Here the PPY(A^-) film as-prepared is considered to contain 0.22 mole of A^- per mole pyrrole unit, based on elemental analysis. Calculated thickness of a PPY layer of 1 μm corresponds to a Q of 2.578 $mCmm^{-2}$. The polypyrrole films of different thickness were deposited on the metal surface (Pt) and for this we used various current densities at constant times.

It is widely accepted that the electropolymerization of pyrrole involves radical coupling with complex reaction kinetics at the electrode surface involving formation of an oxidized polymer [2]. The electrochemical preparation of this polymer is often described as occuring to:



where m is usually between 2 and 4. However, this simple representation belies the true complexity of the process [3]. The electrochemical redox process of PPY may be expressed as:

$$\boxed{\begin{array}{l} -Py^+ - +e^- \rightarrow -Py - +X^- \\ \;X^- \end{array}} \qquad (3)$$

where − py − represents a part of the PPY chain with three to four pyrrole rings, X^- is the counter anion compensating the positive charge on the PPY backbone.

For example in this way, in Figure 1 is presented the cyclic voltammogram of the modified electrode Pt/PPY film doped with Cl^- anions in an aqueous solution of 0.1 M KCl. One can see that at the anodic potential scan a current peak (oxidation peak) is obtained, while at the reverse potential scan a cathodic current peak is obtained. In this case the anodic current peak corresponds to the reaction:

$$PPY/A^- - e^- \rightarrow PPY^+/A^-$$

For the cathodic current peak we presume the reaction:

$$PPY^+/A^- - e^- \rightarrow PPY/A^-$$

In general we can write so:

$$PPY/A^- \xrightarrow[\text{electrolyte froming the"adduct"}]{\text{insertion of the cation } M^+ \text{from the}} PPY/A^-/M^+$$

$$PPY/A^-/M^+ \xrightarrow[\text{oxidation}]{-e^-} PPY^+/A^-/M^+$$

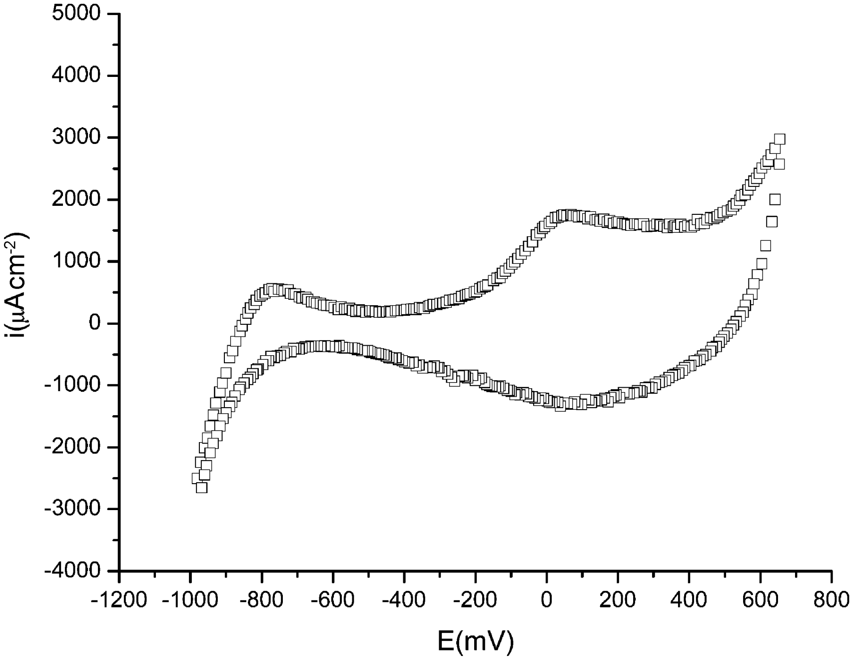


FIGURE 1 The cyclic voltammogram of PPY film doped with Cl^- anions in aqueous solution of 0.1 M KCl at 25°C and a potential scan rate of 40 mvs^{-1}.

At the reverse scan of the potential we have:

$$\mathrm{PPY^+/A^-/M^+} \xrightarrow[\text{reduction}]{+e^-} \mathrm{PPY/A^-/M^+}$$

One or the other step may be favoured depending on the diffusion coefficient of the ionic species in the PPY film. The shape of the voltammetric curve also corroborates this redox mechanism.

Further, the cyclic voltammograms of PPY films synthesized in solutions having different $C_6H_4Na_2O_8S_2$ (1,2 DHBSAS) concentrations are shown in Figure 2.

The shape of the voltammograms consistently change and this indicates that the concentration of the surfactant indeed plays a very relevant role in the electrochemical responses of the PPY/1,2 DHBSAS films (see Table 1). A very sharp reduction peak is shown by the films synthesized from dilute solution, while for those obtained at higher 1,2 DHBSAS concentration the peak becomes progressively broader. Furthermore, for the samples obtained

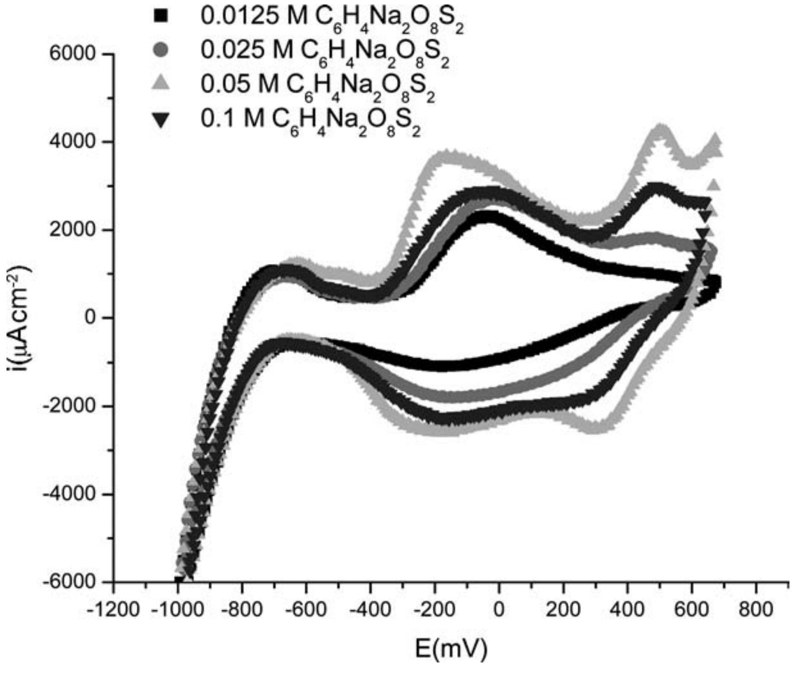


FIGURE 2 The cyclic voltammograms of PPY film doped with 1,2 DHBSAS of different concentrations in aqueous solution of 0.1 M KCl at 25°C and a potential scan rate of 40 mvs^{-1}.

TABLE 1 The Kinetic Parameters of PPY/1,2 DHBSAS Films for Different Concentrations of 1,2 DHBSAS in Aqueous Solution of 0.1 M KCl (the Cycling Electrolyte)

Cycle no	Concentration	Ipa_1 (mA)	Epa_1 (mV)	Ipa_2 (mA)	Epa_2 (mV)	Ipc_1 (mA)	Epc_1 (mV)	Ipc_2 (mA)	Epc_2 (mV)	ΔEp_1 (mV)	ΔEp_2 (mV)
1	0.0125M	4.7	−133	11.6	585	3.47	−260	5.26	334	127	251
1	0.025M	4.07	−142	11.7	598	3.23	−291	5.06	333	149	265
1	0.05M	4.38	−149	12.4	591	3.8	−337	6.1	334	188	257
1	0.1M	4.1	−153	12.0	580	3.43	−300	5.61	340	147	240
5	0.0125M	3.8	20	3.57	497	2.45	−164	2.24	236	184	261
5	0.025M	3.37	−65	5.01	516	2.54	−212	2.81	279	147	237
5	0.05M	3.66	−175	7.1	530	3.32	−270	4.13	345	95	185
5	0.1M	3.39	−142	6.55	522	2.85	−245	3.43	320	103	202
10	0.0125M	2.93	−11	–	–	1.76	−131	–	–	120	–
10	0.025M	2.7	−23	1.82	475	1.8	−138	–	–	115	–
10	0.05M	3.61	−150	4.4	504	2.55	−183	2.54	300	33	204
10	0.1M	2.86	−50	3	493	2.24	−153	1.91	216	103	277

at high concentration there is a modification of the reduction peak upon cycling, with a progressive decrease in sharpness and in total area (see Fig. 3 and Table 2). This effect which has been also noticed by other [4], indicates that the irreversible physico-chemical changes take place during the voltage scan (−1.0 to 0.6 V) of PPY film.

The broad peaks observed in the voltammograms (see Figs. 1, 2 and 3) suggest a complicated redox process for PPY/1,2 DHBSAS. We have observed that PPY doped 1,2 DHBSAS anions (amphiphilic anions) presents an electrolyte-dependent redox process [5–7]. Contrary to what is observed for PPY doped with common low molecular weight inorganic anions (in our case Cl^-), the amphiphilic anion (in our case 1,2 DHBSAS), does not diffuse out from the polymeric matrix. This fact is partially assigned to its size and partially to the compatibility of the polar end with the charged matrix and of the unpolar end with the neutral (reduced) matrix, similar behavior was observed and the other researchers [8].

From Figure 2, one can see that, in this case we obtain two cathodic and two anodic waves. These two peak systems could be explained by a counter ion insertion according to the following scheme:

$$\mathrm{PPY^+/1,2\ DHBSAS^-} \xrightarrow[\text{insertion of } \mathrm{M^+}]{+e^-} \mathrm{PPY^+/1,2\ DHBSAS^-/M^+}$$

$$\xrightarrow[\text{insertion of } \mathrm{X^-}]{-e^-} \mathrm{PPY^+/1,2\ DHBSAS^-/M^+/X^-}$$

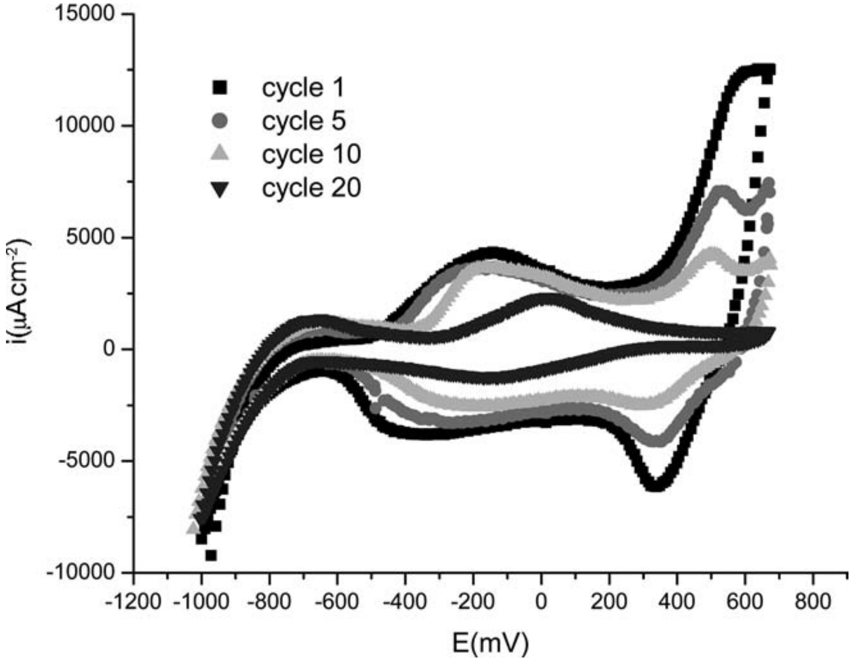


FIGURE 3 The cyclic voltammograms of PPY films doped with 1,2 DHBSAS obtained at different cycles of potential scan.

TABLE 2 The Kinetic Parameters of PPY/1,2 DHBSAS Films in Aqueous Solution of 0.1 M KCl (the cycling electrolyte) at Different Cycles

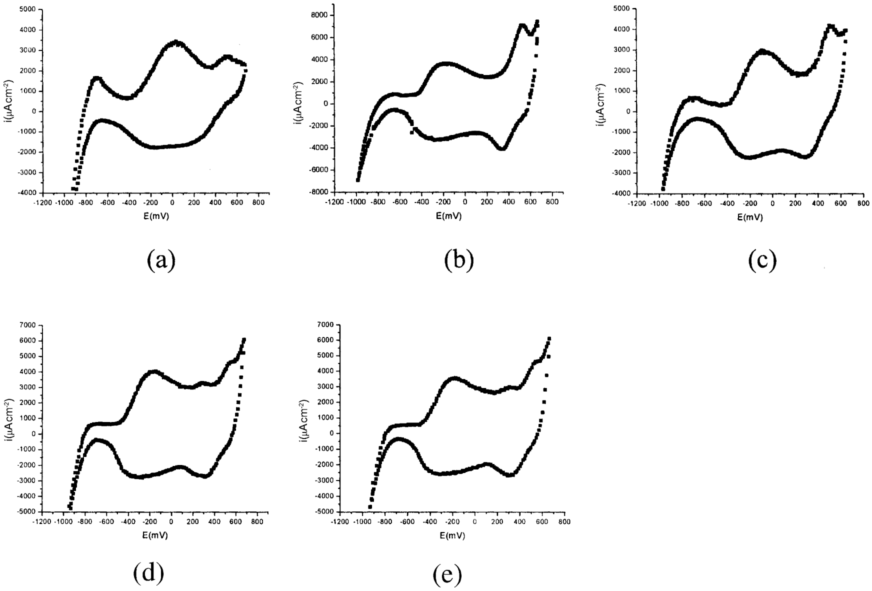
Cycle no	Scan rate ($mV \cdot s^{-1}$)	Ipa_1 (mA)	Epa_1 (mV)	Ipa_2 (mA)	Epa_2 (mV)	Ipc_1 (mA)	Epc_1 (mV)	Ipc_2 (mA)	Epc_2 (mV)	ΔEp_1 (mV)	ΔEp_2 (mV)
1	5	0.94	−128	1.37	450	0.36	−170	0.41	260	42	190
1	10	1.32	−143	1.58	475	0.78	−190	0.68	287	47	188
1	20	2.2	−180	6.07	523	1.4	−270	2.28	350	90	173
1	40	4.3	−140	12.3	570	3.8	−330	6.07	340	190	230
5	5	0.46	−200	0.23	240	0.15	−230	0.09	96	30	144
5	10	1.04	−180	0.5	282	0.34	−206	0.24	110	26	172
5	20	1.92	−130	1.67	458	0.97	−180	0.8	235	50	223
5	40	3.66	−175	7.1	530	3.32	−270	4.13	345	95	185
10	5	0.43	−227	0.12	237	0.09	−247	0.03	50	30	187
10	10	0.96	−198	0.26	270	0.13	−239	0.09	90	41	180
10	20	1.28	−175	0.84	300	0.32	−219	0.24	200	44	100
10	40	3.61	−150	4.4	504	2.55	−200	2.54	300	50	204

$$\mathrm{PPY^+/1,2\ DHBSAS^-/M^+/X^-} \xrightarrow[\text{release of } X^-]{+e^-} \mathrm{PPY/1,2\ DHBSAS^-/M^+}$$

$$\xrightarrow[\text{release of } M^+]{-e^-} \mathrm{PPY^+/1,2\ DHBSAS^-}$$

As we can see from the previous scheme, the reduction process produces the neutral polymer chain, however, the presence of the remaining 1,2 DHBSAS anion leads to the insertion of the cation in order to equilibrate the charge. The cation participation in this process is illustrated by the cyclic voltammograms of the PPY films in solutions of KCl, NaCl, CsCl, $BaCl_2$, and $SrCl_2$, shown in Figure 4. From the analysis of this figure, one can see that, the electrochemical response of the PPY/1,2 DHBSAS film is indeed dependent on the nature of the cation. Changes are observed for the kinetics and reversibility of the process, which are by the sharpness of the main peak, by the number of the peaks and by their height and by their potential separation, ΔEp (see Table 3).

These two peak systems could be explained by a counter-ion insertion. The X^- anion inserted in the polymer matrix would interact with the oxidized sites of the polymer chain. This would change the redox potential of the polymer by the formation of a mixed chain, part of it interacting with the 1,2 DHBSAS anion and part with the X^- anion.



(a) (b) (c)

(d) (e)

FIGURE 4 The cyclic voltammograms of PPY/1,2 DHBSAS films obtained in different cycling solutions (0.1 M KCl; 0.1 M NaCl; 0.1 M CsCl; 0.1 M $BaCl_2$ and 0.1 M $SrCl_2$).

TABLE 3 The Kinetic Parameters of PPY/1,2 DHBSAS Films in Different Aqueous Solutions of Chloride (0.1 M KCl; 0.1 M NaCl; 0.1 M CsCl; 0.1 M $BaCl_2$ and 0.1 M $SrCl_2$)

Cation	Scan rate ($mV{\cdot}s^{-1}$)	Ipa_1 (mA)	Epa_1 (mV)	Ipa_2 (mA)	Epa_2 (mV)	Ipc_1 (mA)	Epc_1 (mV)	Ipc_2 (mA)	Epc_2 (mV)	ΔEp_1 (mV)	ΔEp_2 (mV)
Na^+	20	1.9	−88	1.19	464	0.69	−198	0.66	150	110	314
K^+	20	1.92	−130	1.67	458	0.97	−180	0.8	235	50	223
Cs^+	20	1.5	−40	1.3	470	0.88	−167	0.6	233	127	237
Sr^{2+}	20	1.95	−223	1.91	490	1.26	−255	1.16	314	32	176
Ba^{2+}	20	1.91	−234	1.77	402	1.08	−241	1.05	321	21	81
Na^+	40	3.42	30	2.7	516	1.76	−194	1.46	205	224	311
K^+	40	3.66	−175	7.1	530	3.32	−270	4.13	345	95	185
Cs^+	40	2.97	−80	4.22	518	2.27	−222	2.27	300	142	218
Sr^{2+}	40	4.1	−170	4.65	530	2.75	−300	2.65	312	130	218
Ba^{2+}	40	3.56	−187	4.6	524	2.55	−316	2.7	307	129	217

The cyclic voltammetric responses of PPY/1,2 DHBSAS film in 0.1 M KCl solution are dependent on both the scan rate and the film thickness. For thin films ($< 0.5\,\mu m$) and slow scan rate, the peak separation is constant, $\approx 55\,mV$, indicating that a highly reversible process is maintained in the film. The peak separation (ΔE_p) remained almost constant with scan rates up to $100\,mV{\cdot}s^{-1}$. But when the scan rate was further increased, the peak separation was found to increase. For thicker films, the increasing scan rate resulted in a systematic increase in the peak separation even with as slow scan rates as a few $mV{\cdot}s^{-1}$. For a $2.5\,\mu m$ thick film at $500\,mV{\cdot}s^{-1}$, ΔE_p was about 150 mV. This is much larger than the theoretical value for a diffusion controlled reversible electrode process [9]. Uncompensated IR drop in the film obviously contributes to the increased peak separation. For very thin films ($\approx 0.1\,\mu m$) both anodic and cathodic peak current was found to increase linearly with increasing potential scan rate. Whereas a good linearity between the square root of the scan rate and the peak current was obtained for thick films. Figure 5 shows the cyclic voltammograms of the modified electrode PPY/1,2 DHBSAS film in 0.1 M KCl solution at different scan rates. One can see that, the increasing of the scan rate led in all cases to increase of the height of current peaks and to decrease of the area of these peaks.

CONCLUSIONS

Polymerization of pyrrole in the presence of 1,2 DHBSAS improves both the mechanical properties associated with electrical conductivity and

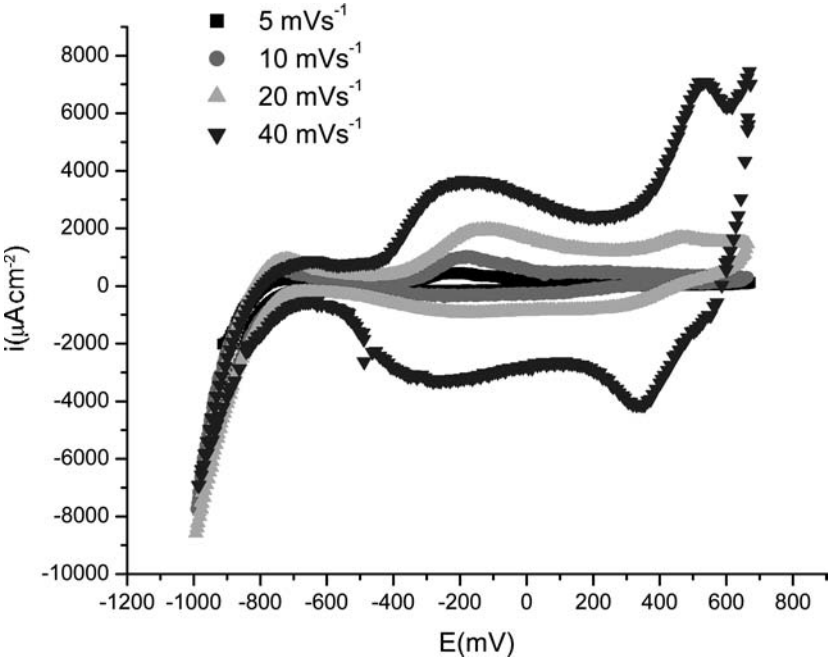


FIGURE 5 The cyclic voltammograms of PPY/1,2 DHBSAS films obtained in aqueous solution of 0.1 M KCl (the cycling electrolyte) and different potential scan rates.

electroactivity of the polymer films. The results indicate that the electrochemical properties of PPY/1,2 DHBSAS film depend very much on the synthesis conditions and on the electrolyte.

The synthesis current density effect is a consequence of the morphological and structural changes induced by the different kinetics of polymer film.

During electropolymerization, pyrrole is oxidized and polymerized to form a highly conjugated positively charged polymer backbone. 1,2 DHBSAS in the polymerization solution enters the film to provide charge neutralization. It has been reported that three or four pyrrole rings share one positive charge [2]. The cation in the solution will therefore take the role of charge compensation during the redox process of the film. In particular, the results inducate that the mechanism of the redox process is complex and may be governed by the diffusion of the cations and anions of the electrolyte.

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