ORIGINAL PAPER

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Electrochemical activity of chemically deposited polypyrrole films

Abstract Conducting polypyrrole (PPY) films are deposited on platinum by chemical oxidation of pyrrole from acid solutions of H_2O_2, $K_2S_2O_8$, $K_2Cr_2O_7$, $FeCl_3$ and $Fe_2(SO_4)_3$. Cyclic voltammograms and charge–potential data are obtained for these PPY films in 0.1 M $LiClO_4$ and 0.1 M Na_2SO4 solutions. Chemically deposited PPY films are electrochemically active and yield oxidation–reduction peak potentials that are similar to those of PPY films electrochemically synthesized in solutions with the same anions. The shape of the cyclic current–potential curves and the charge–potential responses of the chemically deposited PPY depend on the bath composition. The bath determines the counter anion introduced into the PPY film. The physical appearance and thickness of a film depends on the deposition time, acidity and composition of the electroless plating baths.

Keywords Chemical deposition · Cyclic voltammograms · Polypyrrole

Introduction

Many papers discuss the electropolymerization of pyrrole and the properties of the resulting polypyrrole (PPY) film [1]. Less information exists concerning the chemical polymerization of pyrrole in homogeneous solution. Polymerization occurs readily in the presence of different oxidants, such as $FeCl_3$ [2, 3] and ($K_2S_2O_8$ [4]. Numerous studies have been reported about the formation of PPY films on solid surfaces by chemical polymerization of pyrrole (see a recent comprehensive review [5]) and numerous fundamental and applied aspects of the field of electroactive polymers are the subject of a recent monograph [4]. There are many reasons to have a detailed understanding of the chemical deposition process, as there are numerous possible applications of chemically synthesized conducting polymer layers, just as there are for metal films formed by electroless deposition. By analogy, we will refer to chemically synthesized PPY films as electroless films, and electrochemically synthesized films as electrolytic films. Just as for metal films, electrochemical growth of thicker PPY (or other conducting) layers is feasible on electroless PPY films.

There are reports about the polymerization of pyrrole onto printed circuit boards [6, 7] and various textile composites [8, 9]. In these the deposited layers are characterized by conductivity measurements, mass changes and other methods [2] such as mass spectrometry, vibrational spectroscopy [9], Rutherford backscattering spectrometry, scanning electron microscopy and scanning tunneling microscopy [10, 11]. Here we show that the electrochemistry of such films provides a simple diagnostic tool for identifying the doping anion.

In the present work we synthesize electroless PPY films on platinum by polymerizing pyrrole using different oxidants in the presence of different anions and report on the electrochemical characteristics of these electroless PPY films. Our motivation is to identify the counter ion present in electroless PPY films. We propose to do this by matching the electrochemical characteristics of electroless films with those of electrolytic films having known counter anions.

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Experimental

Chemicals

The following compounds are all of a reagent grade and used as purchased: ferric sulfate (Kodak), potassium persulfate (Baker), potassium dichromate, sodium sulfate, hydrogen peroxide,

hydrochloric acid, p-toluenesulfonic acid (TSA) (Fisher), ferric chloride, pyrrole (99%) and lithium perchlorate (Acros). MilliQ water was used and all experiments were done at room temperature.

Polymerization solutions

Five different solutions, as prepared below, were used to make PPY film on platinum:

- 1. 5 mL 1 M of pyrrole (Py) was added slowly while stirring to 50 mL of 30% H_2O_2 containing 1–2 drops of concentrated HCl.
- 2. 20 mL of 0.1 M Py was added slowly while stirring to 50 mL of a solution containing 0.2 M $K_2Cr_2O_7$ and 0.05 M TSA.
- 3. 20 mL of 0.1 M Py was added slowly while stirring to 50 mL of 0.2 M $K_2S_2O_8$.
- 4. 20 mL of 0.1 M Py was added slowly while stirring to 50 mL of 1.5 M $FeCl_3.6H_2O$.
- 5. 10 mL of 0.1 M Py was added slowly while stirring to 50 mL of a saturated solution of $Fe_2(SO_4)_3.H_2O$ containing 5 mL of concentrated H_2SO_4 and 3–5 drops of concentrated HCl.

Procedures

Chemical

Before chemical polymerization, a 1-mm diameter, 3-cm long platinum wire was cleaned, first in a 1:1 concentrated HCl/concentrated H_2SO_4 mixture and then in 4 M NaOH. The wire was next rinsed in water and placed into one of the electroless chemical baths. With two exceptions, smooth black films formed on the Pt surface in 0.2–4 h. The ferric chloride solution gave a film that was blue-black in color, while the ferric sulfate solution gave a dark brown film. Before the electrochemical experiments described below, each PPY-coated platinum wire was rinsed with water and dried in flowing nitrogen.

Electrochemical

The PPY-coated platinum wire was the working electrode, another platinum electrode served as the counter electrode and a saturated calomel electrode (SCE) was the reference electrode in a conventional three-electrode potentiostat experiment. All results are reported versus SCE. The supporting electrolyte used was either 0.1 M $LiClO_4$ or 0.1 M Na_2SO_4.

Rationale for the electrochemical procedure

Chemically and electrochemically polymerized films are potential cycled in the same supporting electrolyte, either 0.1 M $LiClO_4$ or 0.1 M Na_2SO_4. We postulated that the shape of the first cyclic CV and q–E curve would reflect the polymer structure that is characteristic of the counter ion introduced into the PPY during the polymerization, whether it is chemically or electrochemically polymerized. Thus, the electrochemical responses of a chemically synthesized film and an electrochemically synthesized film would only be the same if both films contained the same counter anion. Conversely, films having initially different counter anions would display different electrochemical behavior during the first potential cycle. As shown below, these sorts of comparisons of electrochemical responses provide a valid way to identify the counter anions present in the chemically synthesized PPY films.

Introducing the same counter ion into the chemically polymerized films

A PPY-coated platinum wire was immersed in the supporting electrolyte. Under the experimental conditions used here, the PPY coating is in its oxidized form and contains a counter anion characteristic of the polymerization bath. On potential cycling from an initially positive potential to a negative one, the PPY film is reduced and the counter anion initially present is expelled. On reversing the potential and scanning to more positive potentials, the reduced PPY film oxidizes and the anion characteristic of the supporting electrolyte (perchlorate or sulfate) enters the PPY film. Generally, several potential cycles are required before the CVs stop changing. Presumably this is caused by the slow relaxation of the electroactive polymer to a new "equilibrium" state.

Results and discussion

Comparison of the current–potential and charge–potential curves for the chemically polymerized films

Peroxide bath

Figures 1 and 2 show that the CVs and charge–potential (q–E) plots of electroless PPY films on platinum are characteristic of the polymerization bath used to form the PPY. We make three observations: (1) the PPY film's structure reflects the counter ion introduced into the polymer from the electroless bath; (2) the relaxation of the film's initial structure to the one characteristic of the supporting electrolyte anion is slow on the time scale of the electrochemical experiments; and (3) the oxidation peak potential is ∼0.114 V and the reduction peak potential is −0.32 V, so that film does not exhibit reversible electrochemical behavior.

Figure 1A and Fig. 1B show the CVs and the q–E curves, respectively, obtained in 0.1 M $LiClO_4$ solution for three electroless PPY films that had been made in the dichromate, persulfate and peroxide baths. For all three films, the peak reduction currents in the first CV (0 V to −0.8 V to 0.5 V, scan rate 0.05 V/s) are much higher than in subsequent scans. This behavior is frequently seen in electrolytic polymer films when charge and mass trapping occurs [12]. Also, the oxidation and reduction peak potentials depend on the chemical oxidant used to prepare the electroless film.

The peroxide PPY film gives a high peak anodic current (Fig. 1A, curve 1) that decreases on potential cycling. One rationalization is that some hydrogen peroxide is trapped inside the electroless polymer and is reduced during the first positive-going potential scan. This sort of explanation is used below to rationalize the very large reduction peak currents observed during the first potential cycle for electroless films prepared from dichromate and persulfate baths. A second rationalization is that the film may initially have a structure that makes polymer redox sites more readily available for counter ion (chloride) transfer to the solution on polymer reduction. Then, the polymer's structure relaxes to
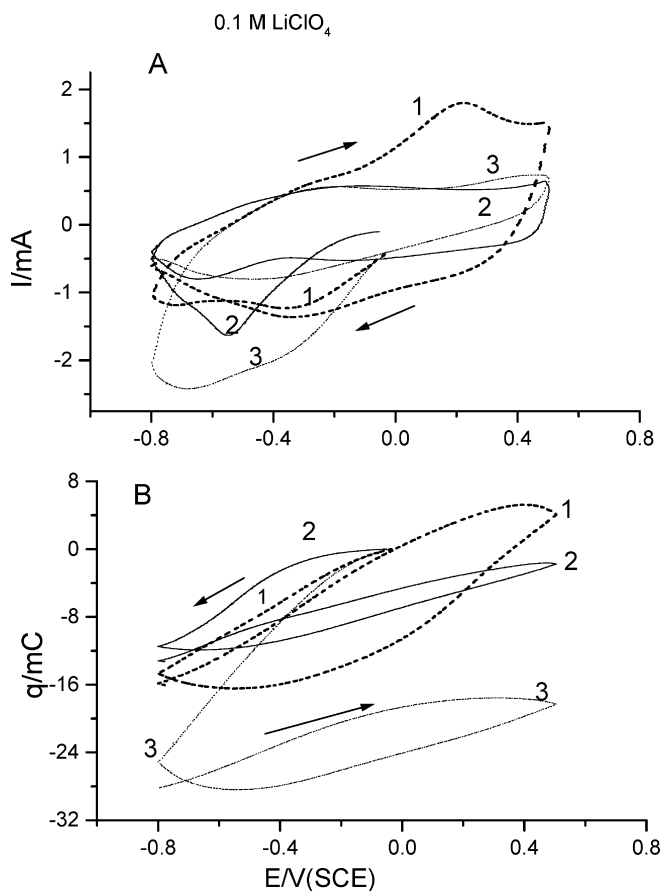
Fig. 1 Cyclic voltammograms (**A**) and charge–potential curves (**B**) for electroless PPY films on platinum in 0.1 M LiClO$_4$. PPY films were made in the following polymerization baths: *1*, H$_2$O$_2$; *2*, K$_2$S$_2$O$_8$; *3*, K$_2$Cr$_2$O$_7$. The potential scan rate is 0.05 V/s

Fig. 2 Cyclic voltammograms (**A**) and charge–potential curves (**B**) for an electroless PPY film on platinum in 0.1 M LiClO$_4$. The potential scan rate is 0.05 V/s. PPY films were made in the following polymerization baths: *1*, FeCl$_3$; *2*, Fe$_2$(SO$_4$)$_3$

that of a reduced polymer form; on further potential cycling the CV displays behavior of a polymer structure more characteristic of a perchlorate ion system.

Of all the PPY films (see below), the peroxide PPY film requires the largest charge to switch between the oxidized and reduced states (Fig. 1B, curve 1). Successive *q*–*E* curves almost overlap, i.e. there is almost no missing charge (no charge trapping) found on further potential cycling.

Dichromate bath

For the dichromate PPY film (Fig. 1A, curve 3), the first CV's peak reduction current is very large and the peak potential shifts negatively compared to the results found in the second and later CVs. These are unusual results and it is difficult for us to explain them if only one redox couple is involved in first potential cycle of the CV.

The peak potentials found in the second and third CVs are −0.25 V for the oxidation and −0.4 V for the reduction peaks. The shape of the CVs and *q*–*E* curves differ from those found for the peroxide PPY film. The very large current for the first reduction CV peak is
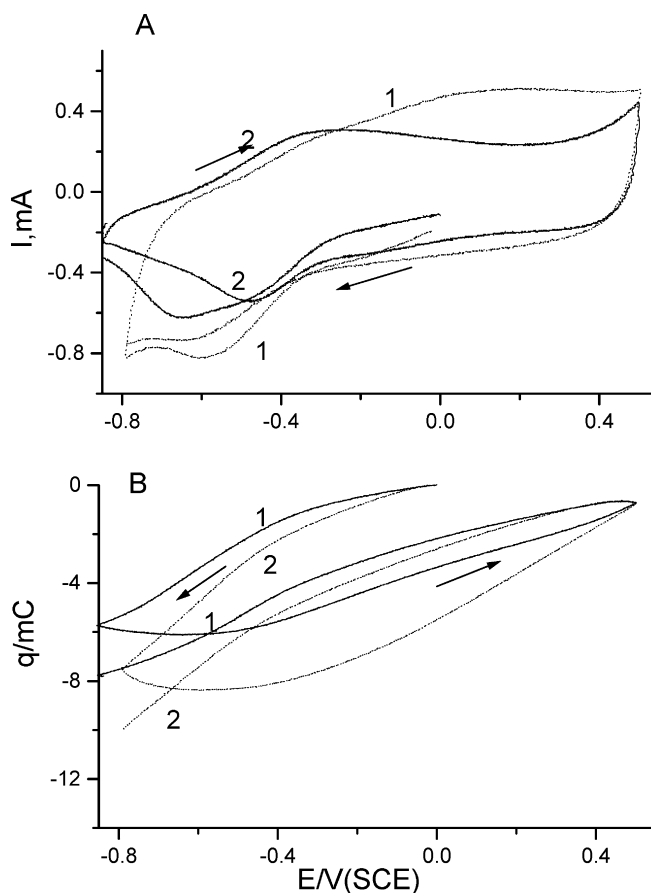
rationalized readily if one assumes that dichromate ion is the counter ion present in the initially oxidized, electroless PPY.

During the initial reduction half-cycle, two processes cause the reduction peak. One is the usual transformation of oxidized to reduced PPY, and the second is the reduction of incorporated dichromate counter anions to form chromic ions. The latter are expelled to maintain electroneutrality within the reduced PPY film. The shift in peak potentials to more positive values after the first potential cycle then is understood as representing the behavior of the electroless PPY polymer system that has incorporated perchlorate counter ions from the bathing solution during electrooxidation. The latter process, the reduction of oxidized PPY containing a monovalent counter anion, would, for electrostatic reasons, be less irreversible than one involving a divalent dichromate anion. Such a film with a divalent counterion would exhibit a positive shift in peak reduction current potential as compared to the one seen in the first potential cycle.

The dichromate PPY film apparently exhibits the largest charge trapping of all the chemically polymerized PVF films (Fig. 1B, curve 3), but this is a spurious result.

The missing charge includes that consumed in the first potential cycle for the reduction of the initially incorporated reducible anion (dichromate), and it is unrelated to a trapping process accompanying a polymer reconfiguration. Similar behavior is reported below for the case when persulfate ion is incorporated into the electroless PPY film.

Persulfate bath

This film undoubtedly contained persulfate anion as the counter ion at the start of the first reduction potential scan (Fig. 1A, curve 2). During the latter scan, there is a large well-formed reduction peak current we ascribe to the reduction both of oxidized PPY to neutral PPY and of persulfate ions to sulfate ions. The latter anions are expelled to maintain electroneutrality in the neutral PPY. After the first potential cycle, this pronounced reduction peak no longer exists because the counter ion is now perchlorate ion and persulfate ions are no longer present in the oxidized PPY. The peak oxidation currents in the CVs for the persulfate PPY film are similar to those for dichromate after the first half-cycle. The peak reduction potential for the second and third scans shifts more negatively to -0.62 V as the PPY adopts a structure characteristic of a perchlorate film. This signifies increasing irreversible electrochemical behavior as the film is cycled.

Ferric baths

Differences exist between the CV and q–E curve found for electroless PPY films made with ferric chloride (Fig. 2A, curve 1) and ferric sulfate (Fig. 2A, curve 2). Films formed in ferric chloride solution are blue-black in color and those formed in ferric sulfate solution are dark brown. The ferric sulfate film's oxidation–reduction peak currents at ~-0.35 V and ~-0.45 V, respectively, are more well defined compared to the chloride film's peaks. In the latter case, only the chloride film's peak reduction potential at ~0.50 V is sufficiently well defined to report it. The sulfate film's peak reduction and peak oxidation potentials are closer to each other, -0.35 V and -0.45 V, than any of the other electroless PPY films, i.e. the ferric sulfate PPY film is *less* irreversible than all the other PPY films. We also note that the more charge is missing on potential cycling the ferric chloride PPY film than is for the case of the ferric sulfate PPY film. These differences in charge trapping clearly demonstrate that the two films are structurally different and the structural polymer reorganizations previously postulated to underlie them [11] are "frozen" out when sulfate ion is the counter anion. The latter suggests (1) that a sulfate ion, by virtue of its high charge density compared to chloride ion, causes electrostatic cross-linking in oxidized PPY and (2) that the reduced PPY does not relax from its oxidized structure on the time scale of the potential cycle. Thus, the partners in the redox process

for a sulfate film do not have structures that are very different, and consequently the large overpotentials required by electron transfers between redox partners of very different structures do not come into play.

We postulate that the colors of the ferric chloride and sulfate PPY films differ from the black color of the other PPY films because these films are not as fully oxidized as the others. Consequently, to test this hypothesis, these films were potential cycled in 0.1 M $LiClO_4$ solutions to more positive potentials than those used for the other films. Figure 3 shows the CVs obtained with the ferric chloride PPY film and Fig. 4 shows the CVs for the ferric sulfate film. Cycling the ferric chloride film to 0.7 V (Fig. 3A, curve 2) changes the shape of the oxidation peak slightly; however, the reduction peak currents increased, more charge became involved in the peak current process, the charge drift decreased (Fig. 3B, curve 2), and the films darkened to a black color. However, when the reversal potential shifted to still more positive values, both the current peaks and charge decreased. After five cycles to a 0.9 V reversal potential, the CVs in the *less* positive potential regions are different (Fig. 3A, curve 3) compared to the initial CVs (Fig. 3A, curve 1). Analogous behavior is observed for the ferric sulfate films (Fig. 4A, curves 1 and 2). We
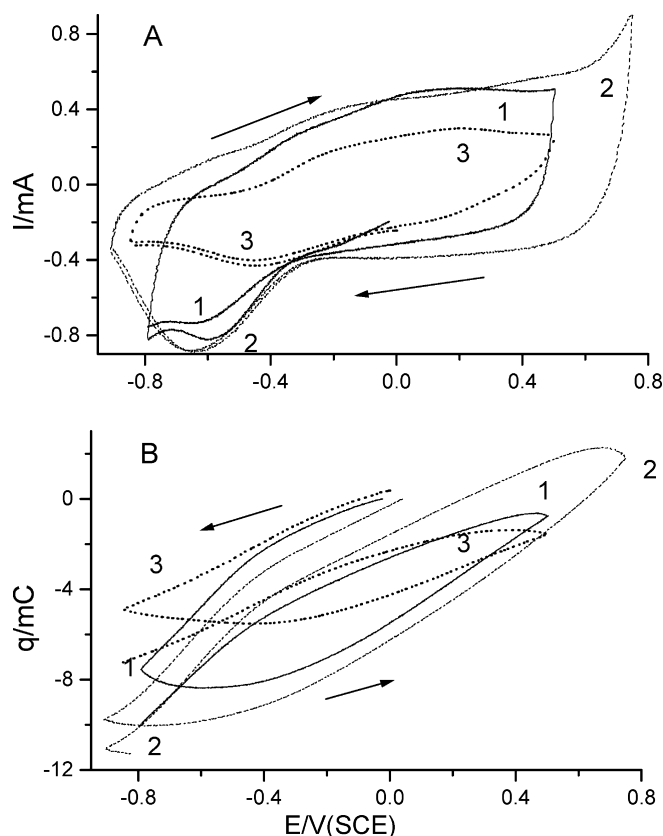

Fig. 3 Cyclic voltammograms (**A**) and charge–potential curves (**B**) in 0.1 M $LiClO_4$ for an electroless PPY film made in $FeCl_3$: *1*, the positive reversal potential is 0.45 V; *2*, the positive reversal potential is 0.7 V; *3*, CVs after cycling several times between -0.9 V and 0.9 V. The potential scan rate is 0.05 V/s
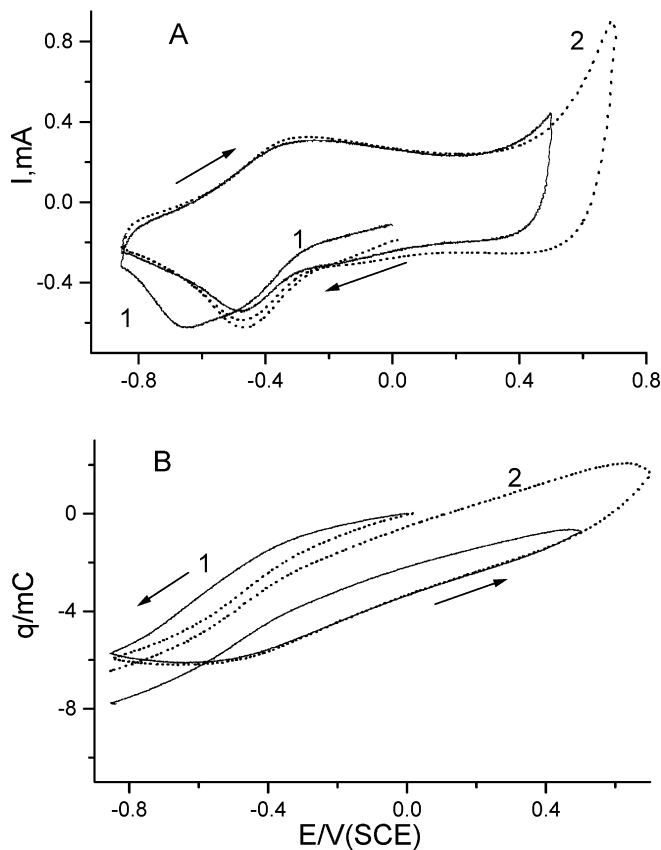
Fig. 4 Cyclic voltammograms (**A**) and charge–potential curves (**B**) in 0.1 M LiClO$_4$ for an electroless PPY film made in Fe$_2$(SO$_4$)$_3$: *1*, the positive reversal potential is 0.45; *2*, the positive reversal potential is 0.6 V. The potential scan rate is 0.05 V/s

Fig. 5 Cyclic voltammograms (**A**) and charge–potential curves (**B**) for an electroless H$_2$O$_2$ PPY film: *1*, in 0.1 M LiClO$_4$; *2*, then holding the film for 5 min in 0.1 M Na$_2$SO$_4$ solution and obtaining the CV in 0.1 M LiClO$_4$; *3*, then in 0.1 M Na$_2$SO$_4$ doping solution. The potential scan rate is 0.05 V/s

ascribe these results to destructive electrooxidation of the electroless PPY film at the very positive potentials.

The effect of repetitive potential cycles was determined for the ferric chloride PPY film (Fig. 3A, curve 3). The charge participating in the oxidation and reduction processes initially increased when the positive reversal potential of the CV extended to 0.7 V, supporting the idea that the less-than-black color of the ferric electroless PPY films represented incompletely oxidized PPY.

Effect of controlled counter ion exchange on the CVs

The above-described experiments provide strong evidence that the different counter anions introduced into the PPY films during chemical polymerization cause the observed peak current and peak potentials differences. To further test our model, we compare the electrochemical responses of electroless and electrolytic PPY films caused to contain the same counter anion. This is done by soaking the electroless films in solutions containing lithium perchlorate or sodium sulfate. Then, the various electroless PPY films are potential cycled in lithium perchlorate and in sodium sulfate supporting electrolytes. We assume that this procedure converts the
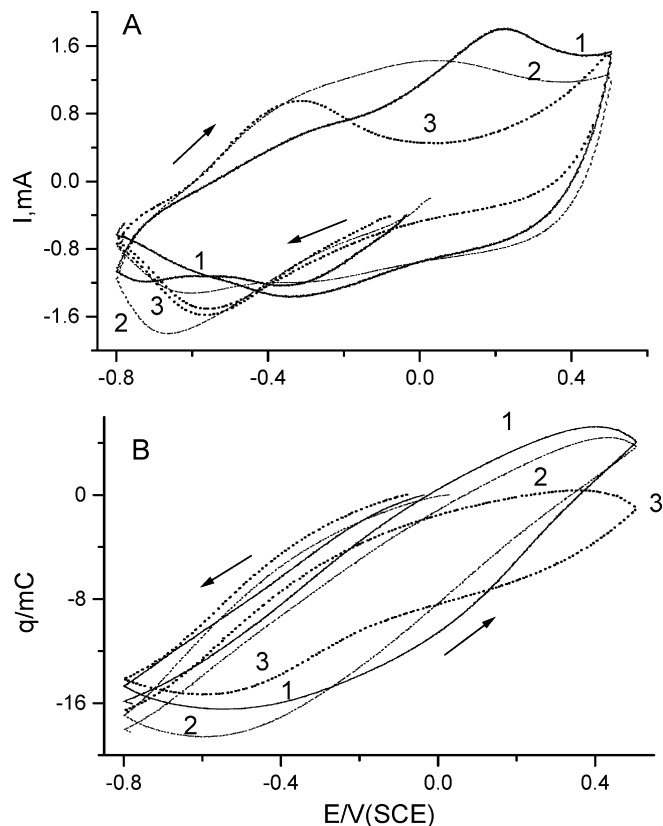
electroless and electrolytic films, initially containing different counter anions, to their perchlorate or sulfate forms. Thus, the observed differences in peak potentials of an electroless PPY film in the above experiments will change from that required by the structure imposed by the original counter ion toward the structure required by perchlorate or sulfate anions.

For example, to test this assumption, a CV of the electroless peroxide PPY film is run in 0.1 M LiClO$_4$ in order to replace the film's chloride counter ions (originating from HCl in the polymerization bath) with perchlorate counter anions (Fig. 5A, curve 1). Then, the film is held for 5 min in 0.1 M Na$_2$SO$_4$ and a CV (Fig. 5A, curve 2) and q–E curves (Fig. 5B, curve 2) are recorded in 0.1 M LiClO$_4$. Next, the same film is potential cycled in 0.1 M Na$_2$SO$_4$ solution (Fig. 5, curve 3). The influence of the SO$_4^{2-}$ ion is evident on comparing both the I–E and q–E curves in these supporting electrolytes. We find a smaller charge change (less charge trapping) between the oxidized and reduced peaks in the case of doping with sulfate counter anions (Fig. 5B, curve 3) as compared to perchlorate (Fig. 5B, curve 1). Again, we attribute this difference in charge trapping to the electrostatic influence of the sulfate anion on PPY's structure, which slows the reconfiguration of PPY.
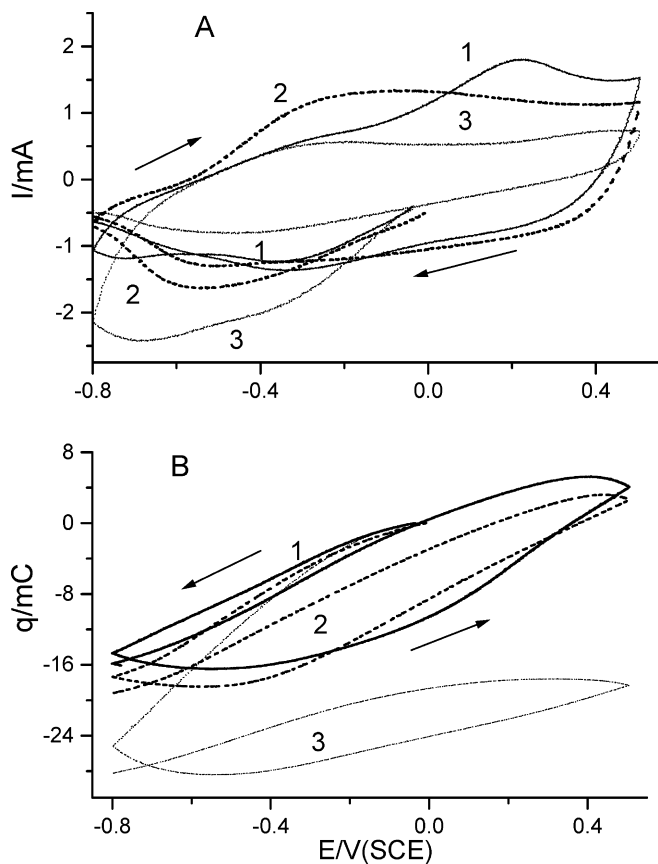
Fig. 6 Cyclic voltammograms (**A**) and charge–potential curves (**B**) in 0.1 M LiClO$_4$ for electroless PPY films: *1*, made in H$_2$O$_2$; *2*, after holding the H$_2$O$_2$ PPY film in Cr$_2$(SO$_4$)$_3$; *3*, made in K$_2$Cr$_2$O$_7$. The potential scan rate is 0.05 V/s

Fig. 7 Cyclic voltammograms (**A**) and charge–potential curves (**B**) for different electroless PPY films in different doping solutions: *1*, H$_2$O$_2$ PPY film in 0.1 M Na$_2$SO$_4$; *2*, K$_2$S$_2$O$_8$ PPY film in 0.1 M LiClO$_4$; *3*, K$_2$S$_2$O$_8$ PPY film in 0.1 M Na$_2$SO$_4$. The potential scan rate is 0.05 V/s

Anion effects are also observed when the peroxide PPY film is held for 3 min in 0.1 M Cr$_2$(SO$_4$)$_3$ (pH > 4) (Fig. 6A, curve 2). Then, the peak potentials in the CV become similar to the one found for a dichromate PPY film (Fig. 6, curve 3). An analogous anion effect is observed in case of the persulfate PPY film (Fig. 7A). The CV for this film in 0.1 M Na$_2$SO$_4$ solution exhibits a smaller shift of the peak potentials, but the current peaks became better defined (Fig. 7A, curves 2 and 3). Differences between solutions containing the same anion but a different cation are caused by the well-known nonpermselective behavior of PPY [13].

We suggest that the mechanism for the formation of the PPY film on platinum differs from the one that causes film formation on a nonconducting surface such as a textile, silica or other insulating surfaces. For a conductor such as platinum, both the cathodic half-reaction for the reduction of the oxidant in solution and the anodic half-reaction for the oxidation of pyrrole can proceed at a significant rate. Then, the conducting surface electrocatalyzes the polymerization process to form the polymer film. Subsequent growth of the conducting polymer film continues with the film acting as the electrocatalytic surface. This mechanism is analog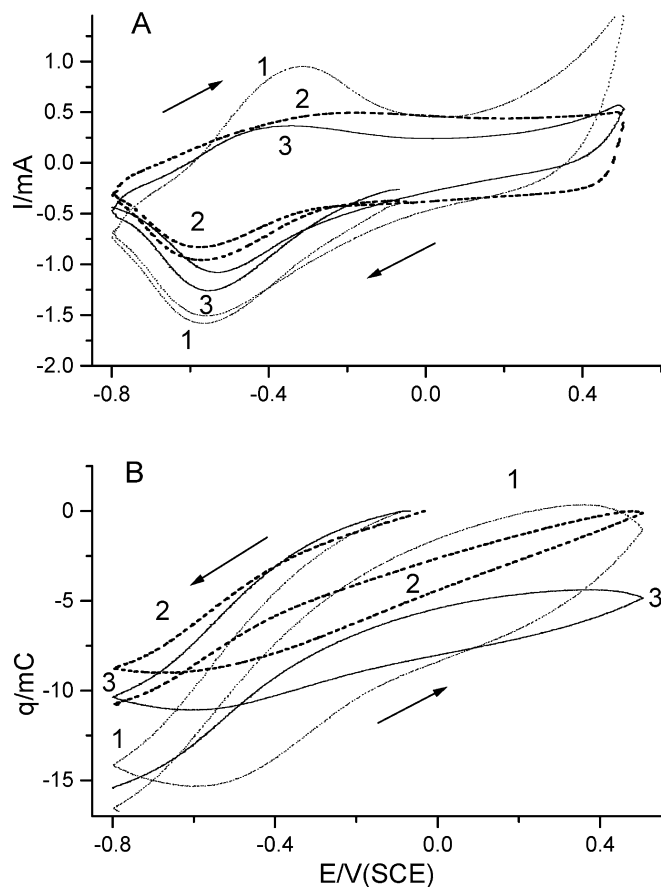ous to the one for electroless deposition of metals on other metals, or on insulating substrates treated to nucleate the initial deposition of the metal that one wishes to deposit.

Conclusions

Several chemical methods produce smooth, electroactive PPY films on platinum. Polymerization of pyrrole to form PPY films on platinum is successful using hydrogen peroxide, potassium dichromate, potassium persulfate, ferric chloride or ferric sulfate as oxidants. These PPY films are electrochemically active and exhibit cyclic voltammetric oxidation and reduction currents in 0.1 M LiClO$_4$ and 0.1 M Na$_2$SO4 solutions. The counter anions present in oxidized PPY films produced by chemical synthesis are identified by comparing the voltammetry these films with those of electrochemically synthesized PPY containing known counter anions. Peak potentials and charge changes in the films depend on the counter (doping) anion initially introduced during the polymerization process. Electrochemical approaches provide a simple way to identify

560

counter ions introduced into chemically polymerized electroactive polymer films.

References

1. Linford RG (ed) (1990) Electrochemical science and technology of polymers, vol 2. Applied Science, London, pp 166–173
2. Ley J, Cai Z, Martin CR (1992) Synth Met 46:53
3. Gottesfeld S, Uribe FA, Armes SP (1992) J Electrochem Soc 139:14
4. Skotheim TA, Elsenbaumer RL, Reynolds JR (eds) (1998) Handbook of conducting polymers, 2nd edn. Marcel Dekker, New York
5. Malinauskas A (2001) Polymer 42:3957
6. Saurin M, Armes SP (1995) J AppI Polym Sci 56:41
7. Hearn MJ, Fletcher IW, Church SP, Armes SP (1993) Polymer 34:262
8. Gregory RV, Kimbrell WC, Kuhn HH (1989) Synth Met 28:C823
9. Hearn MJ, Fletcher IW, Church SP, Armes SP (1993) Polymer 34:262
10. Armes SP, Aldissi M, Hawley M, Beery JG, Gottesfeld S (1991) Langmuir 7:1447
11. Armes SP, Gottesfeld S, Beery JG, Garzon F, Mombourquette C, Hawley M, Kuhn HH (1991) Mater Chem 1:525
12. Jureviciute I, Bruckenstein S, Hillman AR (2000) J Electroanal Chem 488:73
13. Bruckenstein S, Brzezinska K, Hillman AR (2000) Phys Chem Chem Phys 1221