ELECTROCHEMICAL PREPARATION OF POLY(VINYLFERROCENIUM)-PERCHLORATE-POLYANILINE COMPOSITE-MODIFIED PLATINIUM ELECTRODE IN METHYLENE CHLORIDE

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A new surface based on poly(vinylferrocenium)perchlorate-polyaniline ($PVF^+ClO_4^-$-PANI) composite-modified platinum electrode was prepared electrochemically to combine the electrocatalytic properties of an intrinsically conducting polymer and a redox polymer. The composite film was synthesized as a bilayer from individual polymerization solutions. Furthermore, $PVF^+ClO_4^-$ and PANI polymers were simultaneously deposited as a mixture from a methylene chloride solution containing PVF polymer and aniline monomer on Pt electrode. When $PVF^+ClO_4^-$ and PANI were codeposited by cycling the potential between 0.20 and 1.80 V vs Ag|AgCl, these polymers were encapsulated within each other. The encapsulation of $PVF^+ClO_4^-$ inside the growing PANI polymer provided the retainment of $PVF^+ClO_4^-$ on the electrode surface even if it was in dedoped form (PVF). This composite film was characterized by cyclic voltammetry, FTIR, SEM and conductivity measurements. The response of the composite film to catechol and hydroquinone was investigated by chronocoulometry in aqueous medium. It was found that the increase in charge consumption for catechol and hydroquinone was observed up to 7.5 and 5.0 times, respectively, when compared to that of PANI film. This might be due to the presence of $PVF^+ClO_4^-$ in the composite film, which played an important role in accelerating the electron transfer.

Keywords: Conducting materials; Cyclic voltammetry; Electrochemistry; Electropolymerization; Coating; Composite; Conducting polymer; Polyaniline; Poly(vinylferrocene).

Polyaniline (PANI) is one of the most extensively investigated intrinsically conducting polymers with commercial significance due to its high conductivity, good redox reversibility and stability in aqueous solutions and air for its applications in rechargeable batteries and environmental stability, as well as ease of synthesis[1–4]. PANI has many application areas such as

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electrochromic displays, electrocatalysis, and sensors[5–7]. Electropolymerization of aniline is usually carried out in aqueous acid solution. One of the major disadvantage of aqueous media is degradation of the polymer due to the hydrolysis of oxidized PANI (pernigraniline form)[8,9]. Stable, electroactive and conductive polyaniline films were prepared in non-aqueous medium such as acetonitrile and propylene carbonate[10–13]. Up to the recent researches, no study has been conducted about the electrosynthesis of PANI in non-aqueous methylene chloride medium.

Due to its electron-transferring abilities, ferrocene species has an application as "redox mediator" in amperometric biosensors, especially in those based on conducting polymer matrices[14]. The most successful means of incorporating ferrocene moieties involves covalent binding to the polymer backbone. Polypyrrole, poly(cyclopentadithiophene) and polyaniline have previously been employed in this regard[15–18].

Redox polymer-modified electrodes have been widely investigated because of their potential application areas such as electrocatalysis, sensors, energy conversion and storage, electronic displays and devices, and reference electrode systems[19–21]. Modified electrodes based on poly(vinylferrocene) (PVF) can, for example, be employed as electrocatalysts and sensors[22–24]. The oxidized form of this electroactive polymer (PVF^+) can be immobilized on the electrode surface. The PVF^+-modified platinum electrode was prepared by electrooxidation of PVF on platinum electrode at 0.70 V vs Ag|AgCl electrode in methylene chloride/tetra-*n*-butylammonium perchlorate solvent/supporting electrode system[25]. Perchlorate ions (ClO_4^-) in the structure of TBAP are incorporated into the polymer structure as a counter ion as shown in the equation below.

$$PVF + ClO_4^- \rightarrow PVF^+ClO_4^- + e^-$$

The color of $PVF^+ClO_4^-$ film is green and the color of PVF solution is yellow[26].

In the present study, in order to combine electrocatalytic properties of an intrinsically conducting polymer and a redox polymer, the film containing PANI and $PVF^+ClO_4^-$ was electrochemically prepared as bilayers from individual polymerization solutions and was also codeposited from a methylene chloride solution containing PVF polymer and aniline monomer on Pt electrode. PVF polymer in composite film was used as an electron transfer mediator in the electrochemical oxidation of compounds due to its perfect reversible redox properties. Optimum conditions were identified to prepare composite film without $PVF^+ClO_4^-$ removed during the analysis procedures.

In the literature, to the best of our knowledge, there is no such study about the electrosynthesis of the composite film containing PANI and $PVF^+ClO_4^-$ in non-aqueous methylene chloride medium.

EXPERIMENTAL

PVF was synthesized using the method of chemical polymerization of vinylferrocene (Sigma–Aldrich)[27]. 4.24 g of vinylferrocene (Aldrich), 5.00 ml of benzene (BDH, Analar) and 0.0328 g of initiator 2,2′-Azo-bis(2-methylpropionitrile) (AIBN) (Alfa) were charged to a Carious tube. The resulting solution was subjected to several freeze-thaw cycles to degas the solution and it was lyophilized to remove the benzene. The tube was then sealed in vacuum, and as well as the polymerization was carried out at 70 °C for 20 h. The resulting polymer was dissolved in benzene and reprecipitated into methanol (Merck). PVF was dried at 60 °C under vacuum for 24 h.

Aniline (Riedel–de Haen) was distilled under vacuum before use. Methylene chloride (Riedel–de Haen) which was purificated[28] was used to prepare polymerization solutions and kept under a nitrogen atmosphere (BOS). The polymerization solution was deoxygenated by bubbling pure nitrogen gas before electrochemical experiments. Tetra-*n*-butyl ammonium perchlorate (TBAP) (Sigma–Aldrich) was used as the supporting electrolyte in non-aqueous medium, which was kept under nitrogen atmosphere.

Electrochemical measurements were carried out in a single-compartment three-electrode cell with Pt disc ($A = 7.85 \times 10^{-3}$ cm^2) as working electrode, platinum wire as counter electrode and Ag|AgCl(sat) as reference electrode. For FTIR, SEM and conductivity measurements, Pt foil ($A = 1.0$ cm^2) was used as working electrode. Before each experiment, Pt disc electrode was polished with a slurry of Cr_2O_3 with water, rinsed with triple distilled water, cleaned in ultrasonic bath, rinsed with methylene chloride and dried, respectively. The macroelectrode was cleaned by holding it in a flame for a few minutes. The polymers deposited on Pt electrode were immersed in methylene chloride to remove adsorbed electrolyte, monomer and the soluble oligomers formed during electropreparation of the films and then dried at room temperature before characterization studies. FTIR spectra were obtained using KBr pellets. The dry conductivity values of polymers were measured using the four-probe measuring technique at room temperature. Before measurement, dry pellets were prepared from powdery material of polymers under a pressure of 5 t cm^{-2}. The ohmic contact to the films was made with Au-plated four-probe tips, and at least 10 different current values were used to measure potential drops. Electrochemical studies were carried out with CH Instruments System, Model 660B. FTIR and UV-Vis spectra, SEM images of polymer samples were obtained using Perkin–Elmer Spectrum One B FTIR Spectrometer, Perkin–Elmer Spectrum UV-Vis Spectrometer and Carl Zeiss EVO-50 Scanning Electron Microscopy, respectively.

RESULTS AND DISCUSSION

Preparation of Composite Films Containing $PVF^+ClO_4^-$ and PANI

In non-aqueous methylene chloride medium, $PVF^+ClO_4^-$ and PANI polymers were synthesized as bilayers from individual polymerization solutions

and codeposited from a solution containing PVF polymer and aniline monomer on Pt electrode by potentiodynamic and potentiostatic methods. Methylene chloride/0.1 M TBAP solutions which were containing 1.0 mg ml^{-1} of PVF and 33.0 mM $HClO_4$, 50.0 mM aniline were used to deposit $PVF^+ClO_4^-$ and PANI polymers, respectively. At that present, $PVF^+ClO_4^-$ denoted the polymer film which was electrochemically deposited on Pt electrode. The oxidized form of this electroactive polymer (PVF^+) could be immobilized on the electrode surface in methylene chloride solution by electrochemical method[20,22,25]. $PVF^+ClO_4^-$ polymer consists of PVF and PVF^+ moieties. ClO_4^- in the structure of TBAP was incorporated into the polymer structure as a counter ion. In the preparation processes of PANI/$PVF^+ClO_4^-$ bilayer, PANI film was synthesized potentiostatically on Pt electrode at 0.70 V and also 0.90 V; then $PVF^+ClO_4^-$ film was deposited on PANI film at 0.70 V. On the other hand, $PVF^+ClO_4^-$ /PANI bilayer was obtained by inverting the process. It is known that potentiodynamically-synthesized polyaniline was found to be more electroactive especially in sensor studies[15]. Thus, this method was also used to prepare the polyaniline layers. To prepare the PANI/$PVF^+ClO_4^-$ bilayer, PANI film was synthesized potentiodynamically by scanning the potential between 0.20 and 1.80 V at 100 mV s^{-1} scan rate on Pt electrode; then $PVF^+ClO_4^-$ film was deposited on PANI film at 0.70 V. $PVF^+ClO_4^-$ /PANI bilayer was also obtained by inverting the process.

In order to confirm whether the second layer was coated or not, FTIR spectra of $PVF^+ClO_4^-$/PANI and PANI/$PVF^+ClO_4^-$ bilayer films were taken and compared to those of their homopolymer films. FTIR spectra of homopolymer films were first recorded (Fig. 1, spectra a and b) and then characterized. These characteristic peaks appear in the spectrum of $PVF^+ClO_4^-$ film; –C=C– skeleton stretching in aromatic structure at 1419, 1466 and 1632 cm^{-1}, aromatic –C–H outside of plane bending at 1729 cm^{-1}, aliphatic –C–H stretching at 2851 and 2923 cm^{-1}, –C–H stretching in aromatic pentadienyl cycle at 3100 cm^{-1} [22] (Fig. 1, spectrum a). The FTIR spectrum of PANI film shows similar characteristics to literature reports[29–31], with vibration bands of a doped polyaniline structure. The absorption peaks at 742 and 1142 cm^{-1} are assigned to –C–H bending outside and inside of plane, respectively. If the sample was PANI base, the spectrum would exhibit the main peaks at about 1593 and 1492 cm^{-1}, corresponding to quinone and benzene ring-stretching deformations, respectively. In this spectrum (Fig. 1, spectrum b), the peaks are observed at 1561 and 1492 cm^{-1}. One of these modes shows a red shift from 1593 cm^{-1} to 1561 cm^{-1} as is the case in the study carried out by Blinova et al.[29] This shift indicates that the quinoid

structures in PANI are protonated. The absorption band at 1312 cm^{-1} corresponds to p-electron delocalization induced in the polymer by protonation[29]. The band characteristic for the conducting protonated form is observed at 1243 cm^{-1} and is interpreted as a C–$N^{\bullet+}$ stretching vibration in the polaron structure. Out-of-plane deformations of C–H on 1,4-disubstituted rings are located in the region between 800–880 cm^{-1}. The broad band at 1083 cm^{-1} indicates the presence of positive charges in PANI and $PVF^{+}ClO_4^{-}$ chains[32]. The peak at 625 cm^{-1} is also assigned to Cl–O stretching due to ClO_4^{-}. FTIR spectra of bilayer films were compared to those of homopolymer films. The presence of the bands located at 742, 1142, 1312, 1492 and 1561 cm^{-1} in the spectrum of $PVF^{+}ClO_4^{-}$/PANI bilayer indicated that PANI could be coated on $PVF^{+}ClO_4^{-}$. In the case of PANI/$PVF^{+}ClO_4^{-}$ bilayer, the presence of the bands located at 3100, 1729 and 1419 cm^{-1} in spectrum indicated that $PVF^{+}ClO_4^{-}$ could be coated on PANI (Fig. 1, spectrum c).

In this study, we also investigated the use of these bilayer-coated electrodes in electroanalytical applications, particularly in the cathodic region.

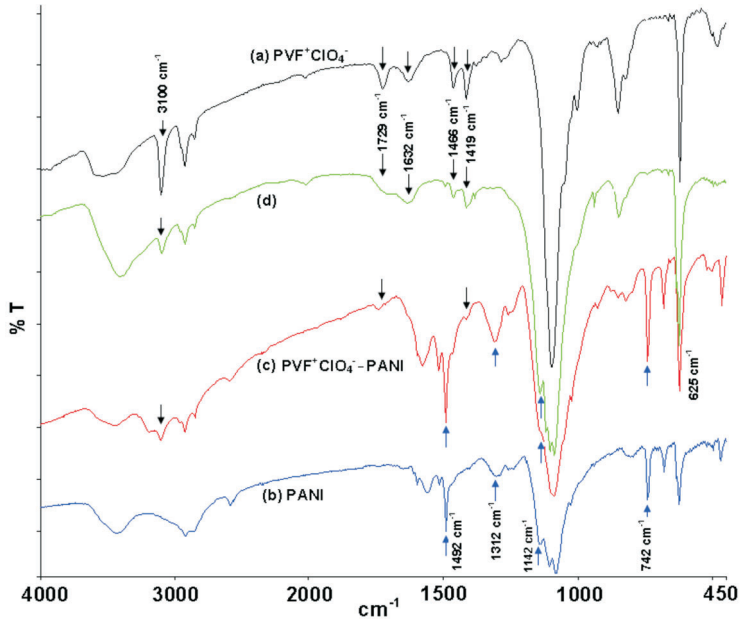

FIG. 1
FTIR spectra for the films: a $PVF^{+}ClO_4^{-}$, b PANI, c $PVF^{+}ClO_4^{-}$-PANI composite and d same composite film after electrolysis at –0.20 V in blank solution

For this purpose, bilayer films were electrolyzed at –0.20 V for 10 min in methylene chloride/0.1 M TBAP solution containing 10 mM $HClO_4$ (blank solution) and then their FTIR spectra were recorded. It was observed that the peak at 3100 cm^{-1}, belonging to the pentadienyl ring of $PVF^+ClO_4^-$, disappeared after electrolysis (Fig. 1, spectrum d). This result demonstrated that PVF^+ in the bilayer film was reduced to PVF, dissolved in methylene chloride, and thus, stripped from the film. Therefore, it was clear that bilayer films were not suitable for electroanalysis purposes.

In order to prepare the composite film without $PVF^+ClO_4^-$ (or PVF) was removed, $PVF^+ClO_4^-$ and PANI were examined for codeposition from a methylene chloride solution containing PVF polymer and aniline monomer by the potentiodynamic method. To this end, the potential window was established. To determine the optimum lower and upper potential values, preliminary studies were performed using $PVF^+ClO_4^-$ and PANI homopolymers, respectively. Electropolymerization of aniline on Pt electrode could not be carried out without $HClO_4$ in methylene chloride/0.1 M TBAP solution containing 50.0 mM aniline by potentiodynamic method. This might be due to unstability of the anilinium cation radical in the absence of $HClO_4$. Therefore, $HClO_4$ was added to the polymerization solutions. The most important species in the growth of the PANI films is the cation radical of aniline[12,32]. The existence of sufficient amounts of protonated aniline in the electrode region where the aniline cation radical is generated provides the necessary conditions for the stability of the cation radicals. Thus proton loss from the cation radical and formation of the neutral aniline radical and its subsequent oxidation to the nitrenium cation are prevented. PANI was synthesized in methylene chloride/0.1 M TBAP solution containing 33.0 mM $HClO_4$ and 50.0 mM aniline by scanning the potential region from –0.20 V to various upper potentials between 1.0 and 1.80 V (Fig. 2). When potential scan was performed from –0.20 V to more anodic potential values, differences in peak currents of the PANI film between successive scans gradually increased (Fig. 2), and the broad oxidation and reduction peaks shifted to more anodic and cathodic values as the film grew, respectively. Figure 3 shows the cyclic voltammetric behavior of these electroactive films in blank solution containing 10.0 mM $HClO_4$. The broad oxidation and reduction peaks of polymer are seen in the figure. As long as there was no loss of electroactivity during the first cycle, the amount of electroactive film deposited could be assumed to be proportional to the charge passed during the oxidative cycle. Thus, the charge was measured during the first oxidative cycle of the cyclic voltammogram of these films in blank solution and the graph of charge measured versus upper potential value was plotted

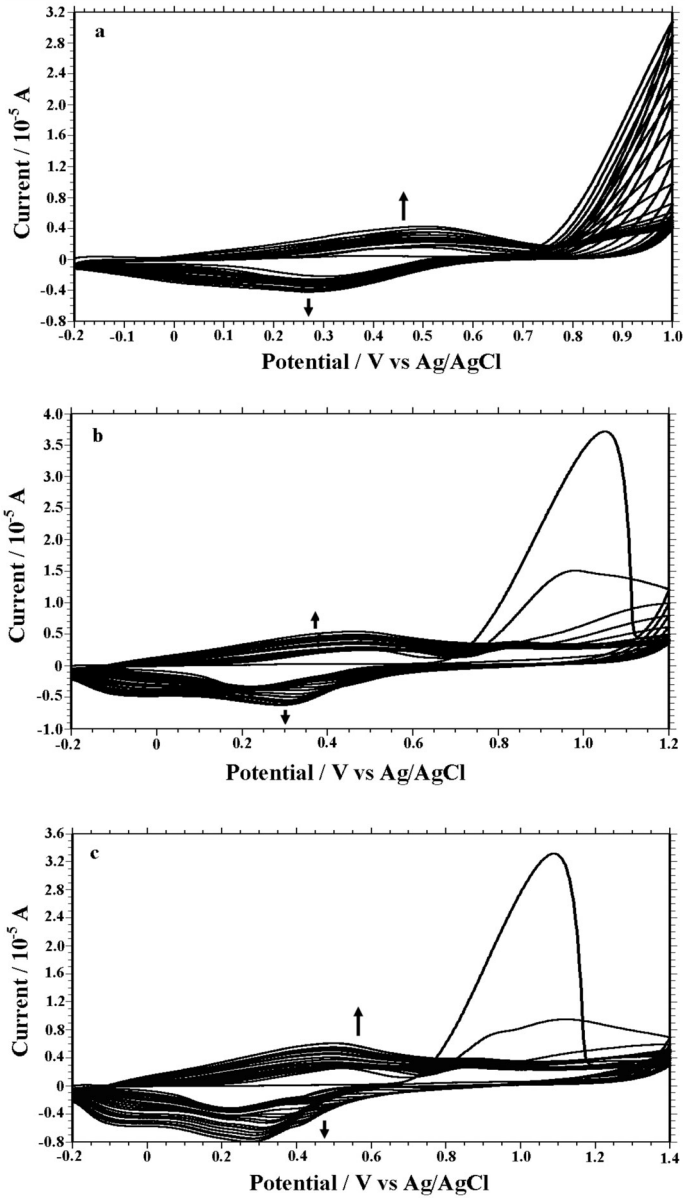

FIG. 2
Cyclic voltammograms recorded during potentiodynamic growth of PANI on Pt electrode in a methylene chloride solution containing 0.100 M TBAP/50.0 mM aniline /33.0 mM $HClO_4$ from –0.20 V to a 1.00, b 1.20, c 1.40, d 1.60 and e 1.80 V vs Ag|AgCl, v = 100 mV s^{-1}

(Fig. 4). It was established that the amount of the electroactive PANI film on Pt electrode increased with increasing upper potential value. As a result, 1.80 V was chosen as the upper potential value.

To determine the optimum lower potential value for the preparation of composite film, $PVF^+ClO_4^-$ film was deposited at 0.70 V in methylene chloride/0.100 M TBAP solution containing 1.0 mg ml^{-1} of PVF by potentiostatically; then these films were scanned from various potentials between 0.20 and –0.20 to 1.80 V in blank solution (Fig. 5). As seen in Fig. 5a, the currents of both reduction and oxidation peaks decrease with increasing number of cycles, after the third cycle the value of peak current approaches to that of blank solution. After the last cycle, green-colored $PVF^+ClO_4^-$ film was not observed on Pt electrode. It could be concluded that all PVF^+ moieties were reduced to PVF and resulting film was stripped

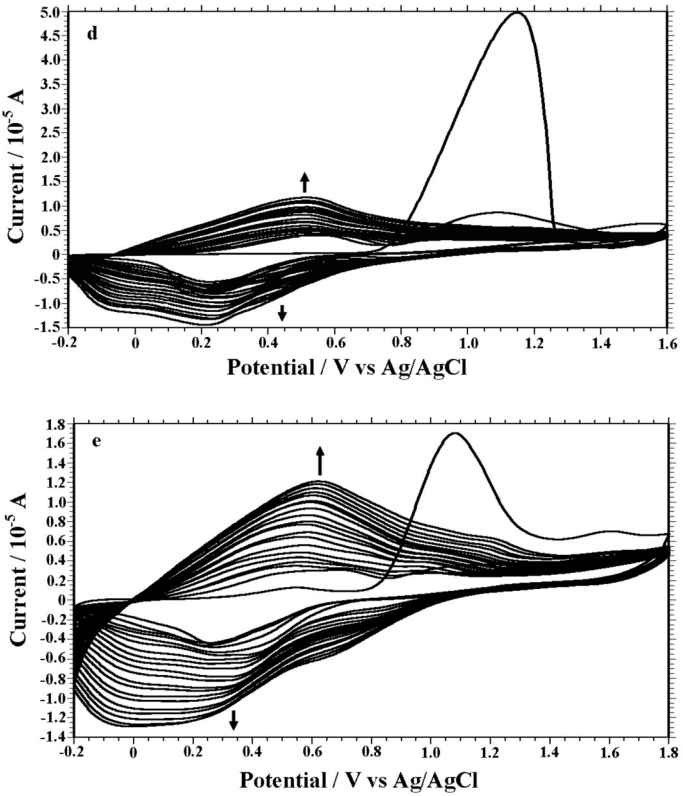

FIG. 2
(*Continued*)

from the surface by dissolution in methylene chloride solution. As cathodic potential shifted to more positive values, the peak current did not decrease more rapidly on successive scans. In the case of 0.20 V, cathodic potential was limited to a value in order not to reduce the film (Fig. 5c). It was recognized that the green film was observed not to strip from Pt electrode even if polycyclic scan was performed. Consequently, the optimum lower potential value was chosen as 0.20 V in order not to remove $PVF^{+}ClO_4^{-}$ polymer from the electrode surface.

As a result, the potential region from 0.20 to 1.80 V vs Ag|AgCl was the most suitable region for potentiodynamic synthesis of composite film.

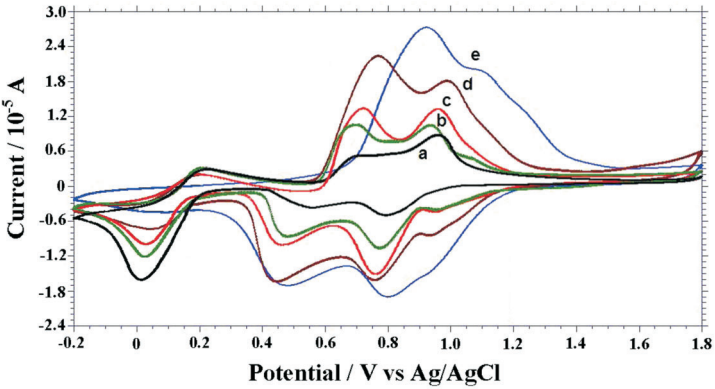

FIG. 3
Cyclic voltammetric behavior of PANI films obtained in Fig. 2 in blank solution containing 10.0 mM $HClO_4$, ν = 100 mV s^{-1}

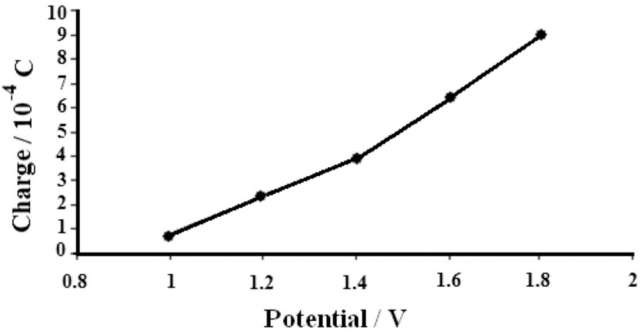

FIG. 4
Plot of the charge passed during the electro-oxidation of PANI films in blank solution containing 10.0 mM $HClO_4$ versus the upper potential applied during electropolymerization

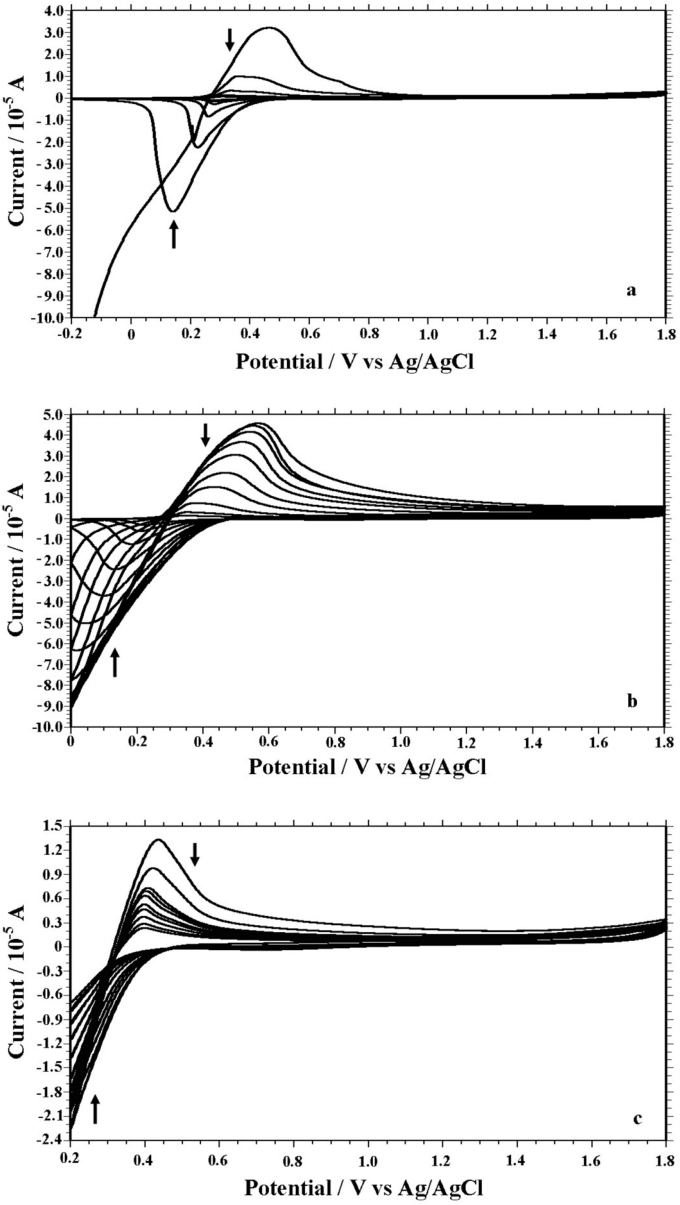

FIG. 5

Cyclic voltammograms recorded from 1.80 V to a –0.20, b 0.00 and c 0.20 V vs Ag|AgCl for $PVF^{+}ClO_4^{-}$ in blank solution ($PVF^{+}ClO_4^{-}$ film deposited at 0.70 V on Pt electrode in methylene chloride solution containing 0.100 M TBAP/1.00 mg ml^{-1} PVF), ν = 100 mV s^{-1}

$PVF^+ClO_4^-$-PANI composite film was deposited on Pt electrode at this potential region at 100 mV s^{-1} scan rate in a methylene chloride solution containing 0.10 M TBAP, 33.0 mM $HClO_4$, 50.0 mM aniline and 1.0 mg ml^{-1} of PVF (Fig. 6). When both the current and the potential of this voltammogram were compared to those of homopolymers obtained under the same conditions, it was clear that the properties of composite film were different from those of homopolymers. Figure 7 shows the cyclic voltammetric behavior of these electroactive films in blank solution containing 10.0 mM $HClO_4$. As can be seen in these voltammograms, the electrochemical behavior of composite film differs from those of homopolymer films; furthermore, the peak current of composite film is higher than that of homopolymer films.

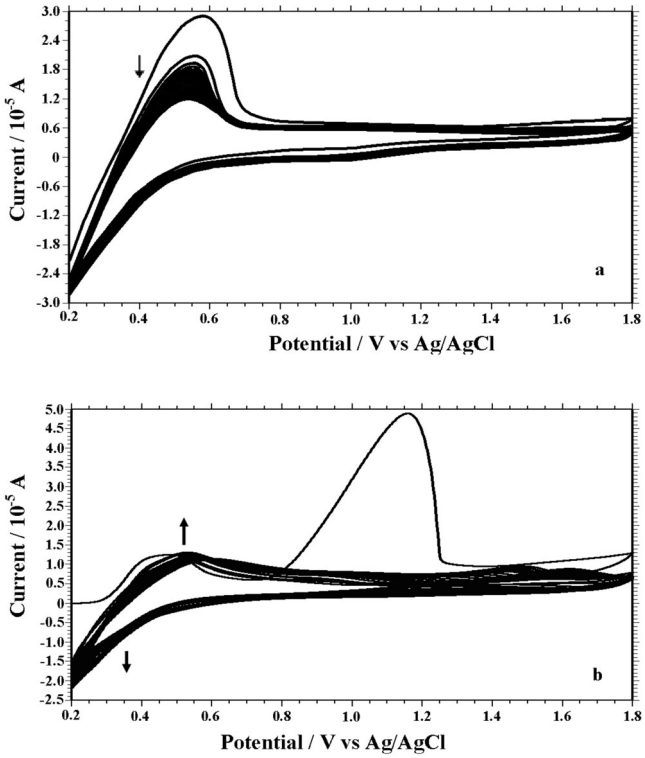

FIG. 6
Cyclic voltammograms recorded during potentiodynamic growth of a $PVF^+ClO_4^-$ in methylene chloride solution containing 1.00 mg ml^{-1} PVF/33.0 mM $HClO_4$ and b $PVF^+ClO_4^-$-PANI composite in methylene chloride solution containing 50.0 mM aniline/1.00 mg ml^{-1} PVF/ 33.0 mM $HClO_4$ on Pt electrode, v = 100 mV s^{-1}

In order to confirm whether composite film contained $PVF^+ClO_4^-$ and PANI or not, FTIR spectrum of composite film was recorded and compared to those of homopolymers (Fig. 1). According to spectrum c in Fig. 1, this composite film contained $PVF^+ClO_4^-$ and PANI polymers due to the presence of absorbance peaks at 3100, 1729, 1419 cm^{-1} and at 1492, 1561, 1312, 1142, 742 cm^{-1}, respectively. Moreover, green-colored composite film was reduced at –0.20 V in blank solution and then its FTIR spectrum was recorded (Fig. 1, spectrum d). As seen in this figure, the peak at 3100 cm^{-1} belonging to the pentadienyl ring of $PVF^+ClO_4^-$ still exists in the spectrum after electrolysis. This means that PVF formed during the electrolyzing was not stripped from the composite film by dissolution in methylene chloride solution. Even if the composite film was deposited in the potential between –0.20 and 1.80 V vs Ag|AgCl, the peak at 3100 cm^{-1} appeared in the spectrum. In other words, PVF formed in the cathodic region was not stripped from the composite film during the deposition. It could be concluded that $PVF^+ClO_4^-$ and PANI polymers encapsulated within each other as a mixture during the deposition of composite film. In addition, among the coatings, the most adhesive film on Pt electrode surface was obtained when PANI and $PVF^+ClO_4^-$ were codeposited. Consequently, the most suitable composite film for electrocatalytic-purpose use is the film deposited from the solution mixture of both PVF and aniline by scanning the potential between 0.20 and 1.80 V.

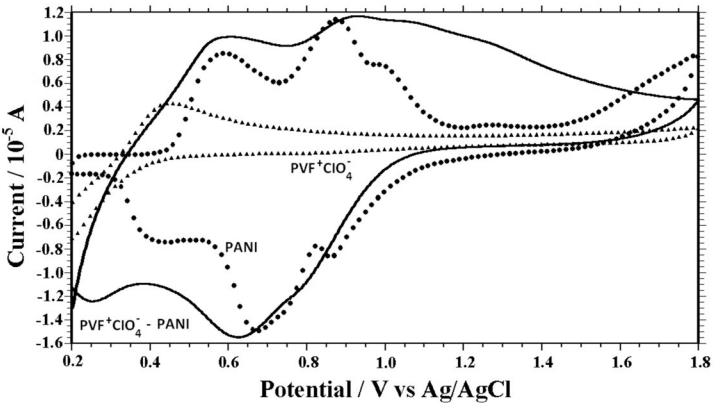

FIG. 7
Cyclic voltammetric behavior in blank solution containing 10.0 mM $HClO_4$ for the films: $PVF^+ClO_4^-$-PANI composite and its homopolymers ($PVF^+ClO_4^-$, PANI) obtained under the same conditions, ν = 100 mV s^{-1}

Also, we prepared $PVF^+ClO_4^-$-PANI composite films containing more PANI. The composite films were deposited on Pt electrode by cycling the potential between 0.20 and 1.80 V vs Ag|AgCl in methylene chloride/0.100 M TBAP solutions containing 33.0 mM $HClO_4$, 1 mg ml^{-1} of PVF and various concentrations between 100 and 200 mM aniline. The cyclic voltammograms of these composite films were taken in blank solution under the same conditions. Then the charges passed during the first oxidative cycle were measured. The highest charge which means the most electroactivitive film was measured with the polymerization solution containing 100 mM aniline. The voltammetric behavior of this composite film in blank solution is similar to the behavior of that prepared from methylene chloride solution containing 50 mM aniline. However, the maximum peak current increased when aniline concentration was 100 mM (23.6 μA) and decreased when it was 150 mM (14.3 μA), due to the domination of oxidized form (polypernigraline) in PANI [32].

As a result, PVF is oxidized at 0.50 V vs Ag|AgCl forming PVF^+ in a methylene chloride solution containing a mixture of PVF polymer and aniline monomer. The existence of PVF^+ moieties in the polymer chains provides the deposition of this electroactive polymer on the electrode surface. Aniline monomer and its oligomers are also oxidized after 0.80 V vs Ag|AgCl in the same medium and afterwards PANI polymer forms. Thus, both polymers are deposited simultaneously on the electrode surface during the potential scanning between 0.20 V and 1.80 V and encapsulated within each other as a mixture. The encapsulation of $PVF^+ClO_4^-$ inside the growing PANI polymer ensures the retainment of $PVF^+ClO_4^-$ in the composite film even if the polymer was in dedoped form (PVF).

Characterization

Conductivity measurements. Conductivity of a film is another important factor in electrocatalytic studies. Dry conductivity values of composite films prepared with different amounts of PANI and their homopolymer films deposited under the same conditions were measured by using the four-probe measuring technique and are given in Table I. It got clear by a comparison of conductivity values that the conductivity of composite film is between the conductivities of PANI and $PVF^+ClO_4^-$ homopolymer films. The composite film with highest conductivity was obtained when the aniline concentration was 100 mM in the polymerization solution. When aniline concentration further increased, the emeraldine moieties in the polymer

chains and also the protonation degree of PANI decreased due to the basic property of aniline[3,32,33]. Hence, the conductivity values of films decreased.

Surface morphologies. The morphologies of the composite and homopolymer coatings were investigated by SEM. Figure 8 shows the image of $PVF^+ClO_4^-$, PANI and $PVF^+ClO_4^-$-PANI composite coatings deposited potentiodynamically in methylene chloride medium. PANI homopolymer and $PVF^+ClO_4^-$-PANI composite coatings were obtained in a polymerization solution containing 100 mM aniline. The morphology of $PVF^+ClO_4^-$ exhibits a globular structure. PANI synthesized in acidic methylene chloride medium exhibits a crystalline structure in contrast to other media. The image of $PVF^+ClO_4^-$-PANI composite coating is similar to that of $PVF^+ClO_4^-$ coating. The difference between these two images is the dimension of the particle size. Diameter of globulars varies between 40–400 and 40–700 nm for $PVF^+ClO_4^-$ homopolymer and $PVF^+ClO_4^-$-PANI composite, respectively.

The chemical composition of the composite and homopolymer coatings were investigated by EDS (Fig. 9). The peaks present in EDS spectra and related atoms are: C at 0.24 keV, N at 0.35 keV, O at 0.52 keV, Cl at 2.61 keV and Fe at 6.25 keV. The existence of Cl peak shows the existence of ClO_4^- in

TABLE I
The conductivity values of $PVF^+ClO_4^-$, PANI homopolymers and composite films prepared by scanning from 0.20 to 1.80 V in methylene chloride solution containing 0.100 M TBAP/33.0 mM $HClO_4$ and various concentrations of monomers

Polymerization solution	Conductivity, S cm^{-1}
$PVF^+ClO_4^-$	
1.00 mg ml^{-1} PVF	6.00×10^{-4}
PANI	
50.0 mM aniline	5.20×10^{-2}
100 mM aniline	5.73×10^{-1}
$PVF^+ClO_4^-$-PANI	
1.00 mg ml^{-1} PVF–50.0 mM aniline	1.30×10^{-3}
1.00 mg ml^{-1} PVF–100 mM aniline	2.50×10^{-1}
1.00 mg ml^{-1} PVF–150 mM aniline	9.60×10^{-3}
1.00 mg ml^{-1} PVF–200 mM aniline	1.40×10^{-3}

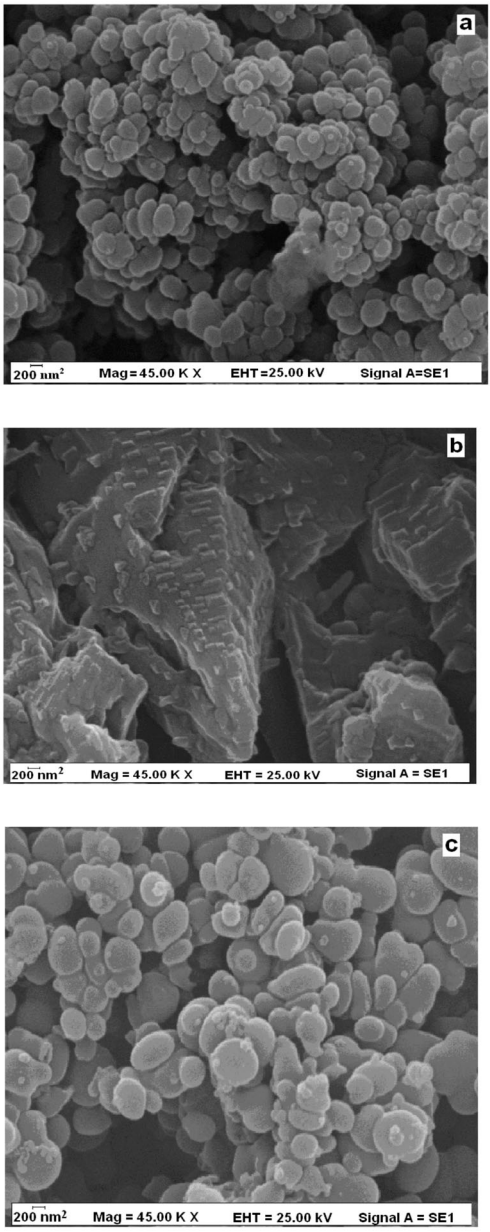

FIG. 8
SEM images of a $PVF^{+}ClO_4^{-}$, b PANI and c $PVF^{+}ClO_4^{-}$-PANI composite coatings

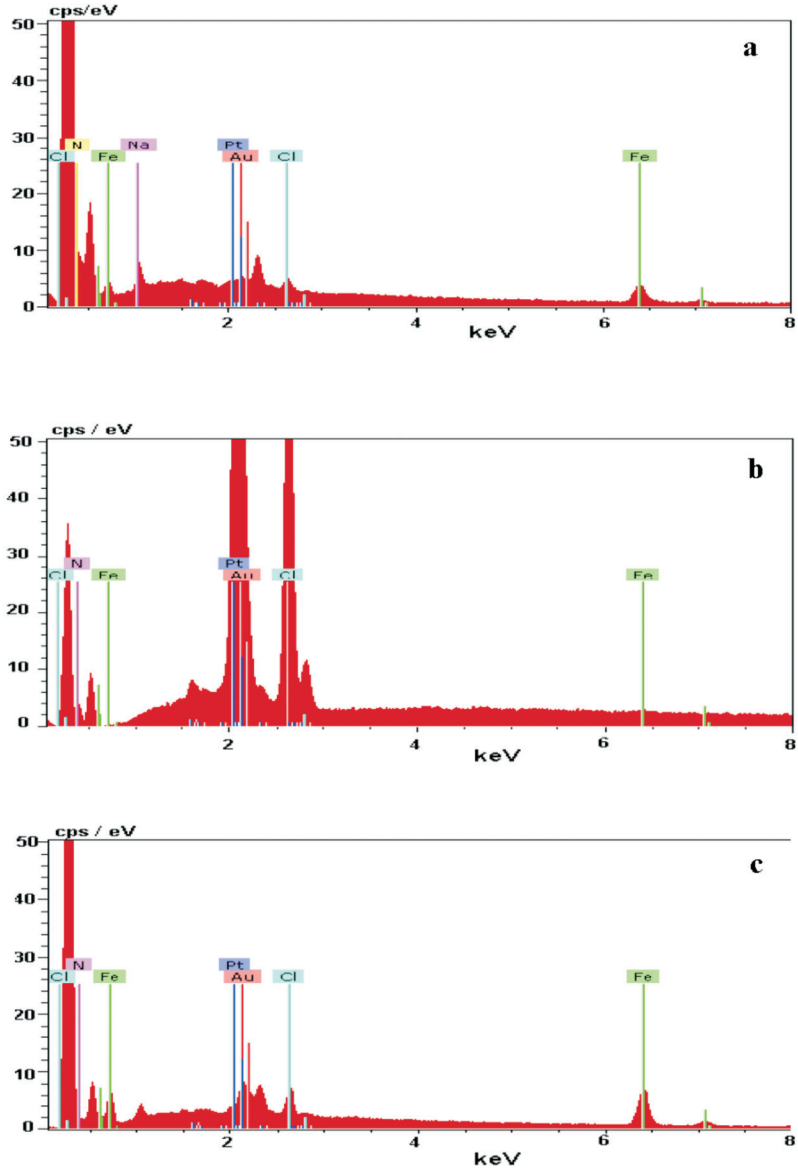

FIG. 9
EDS spectra of a $PVF^{+}ClO_4^{-}$, b PANI and c PANI-$PVF^{+}ClO_4^{-}$ composite coatings

the structure of composite and homopolymers as counter ion. Furthermore, the peak located at 6.25 keV is the evidence of Fe and hence existence of PVF^+ in the composite film.

UV-Vis spectra. Figure 10 shows the UV-Vis spectra of $PVF^+ClO_4^-$-PANI composite film, $PVF^+ClO_4^-$ and PANI homopolymer films deposited on ITO electrodes. For comparison, the spectrum of PVF coated electrode was recorded and given in the same figure. PVF coated electrode was prepared by immersing the ITO electrode into a solution of 1.0 mg ml^{-1} of PVF in methylene chloride and following solvent evaporation[34]. As it shown in this figure, one can speak of three major absorption bands that can be singled out in the UV-Vis spectrum of $PVF^+ClO_4^-$. The first band with a pronounced maximum about 450 nm corresponds to π–π* electronic transitions and the other absorption bands correspond to the oxidized film fragments in deposited film as $PVF^+ClO_4^-$ about 650 and 1200 nm. In the UV-Vis spectrum of PANI film, the polaron band at about 410 nm [35,36] and bipolaron band after 800 nm are clearly observed. The UV-Vis spectrum of composite film differs from those of homopolymer films. As we can see, that both PANI and $PVF^+ClO_4^-$ polymers are present in the composite film.

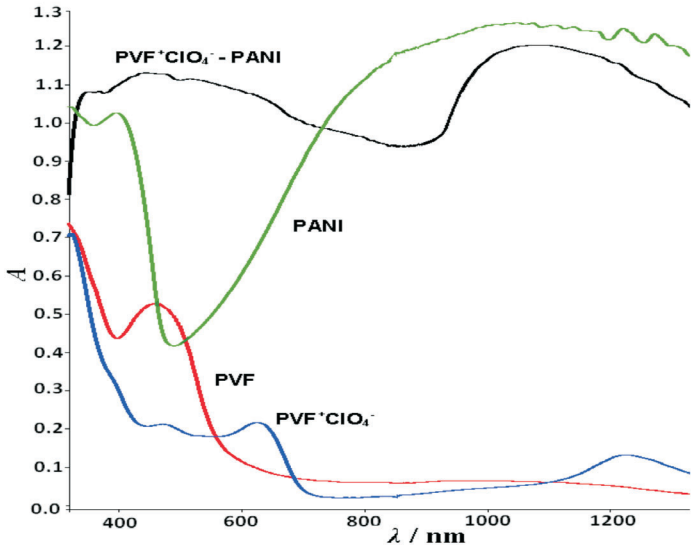

FIG. 10
UV-Vis spectra for the films: PVF, PVF^+ClO_4, PANI homopolymers and $PVF^+ClO_4^-$-PANI composite

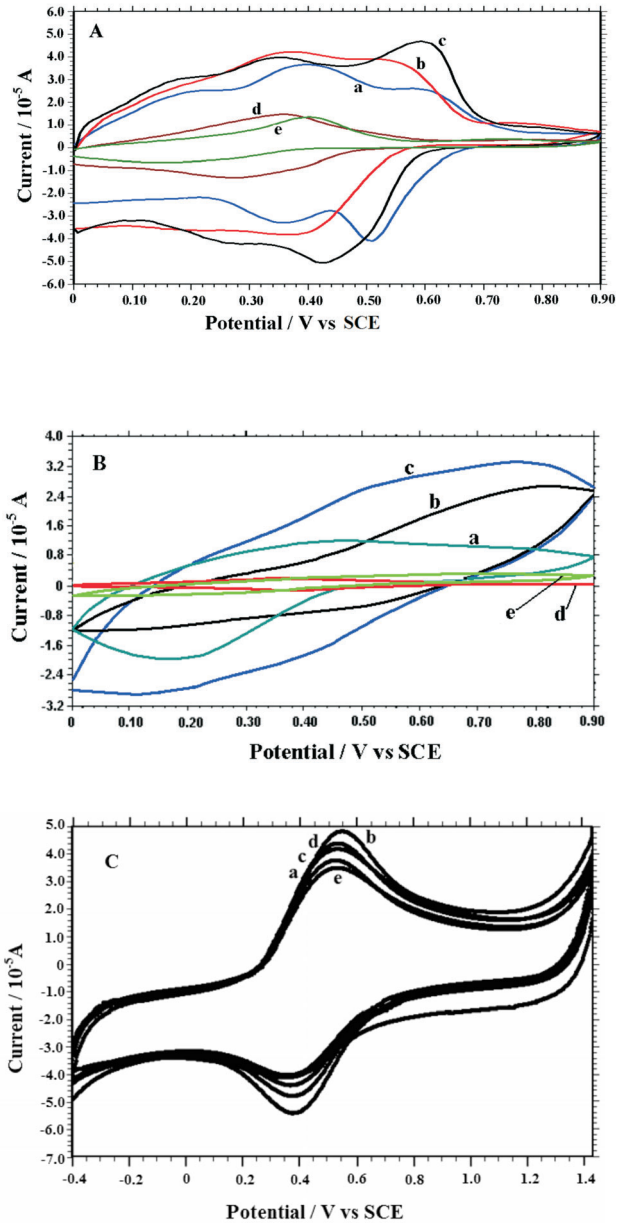

FIG. 11

Cyclic voltammograms of A PANI, B $PVF^+ClO_4^-$-PANI and C $PVF^+ClO_4^-$ films in aqueous $NaHSO_4/Na_2SO_4$ solution at pH values of a 2.0, b 3.0, c 4.0, d 4.5 and e 6.5, ν = 100 mV s^{-1}

Effect of pH

pH of the solution has a significant influence on the stability of polymer film. PANI is electrochemically active in both aqueous and non-aqueous media at anodic potentials. In general, electroactivity of PANI decreases with increasing pH value of aqueous solution (except self doped polyaniline) and at pH values greater than 5, electroactivity is very limited and does not show any electrocatalytic effect for some species[37,38]. Therefore, the effect of pH on the electrochemical behavior of $PVF^+ClO_4^-$-PANI composite and also homopolymers was investigated in aqueous medium. Figure 11 shows the cyclic voltammograms of composite and homopolymer coatings recorded at different pH values in the solutions of $NaHSO_4/Na_2SO_4$. According to this figure, the electrochemical behavior of $PVF^+ClO_4^-$ is not affected by the pH of solution. $PVF^+ClO_4^-$-PANI composite and PANI homopolymer have the highest electroactivity at a pH value of 4.0. PANI contains the highest amount of leucoemeraldine radical cations ($L^{\bullet+}$) and emeraldine radical cations ($E^{\bullet+}$) at this pH. With increasing pH, PANI polymer and also the PANI polymer in the composite gradually lose their electroactivity. This result could be attributed to the fact that $L^{\bullet+}$ and $E^{\bullet+}$ are very unstable in this medium and easily converted to pernigralinine (P)[3,32,33].

$$L^{\bullet+} + 4\ OH^- \rightarrow P + 4\ H_2O + 3\ e^-$$

$$E^{\bullet+} + 2\ OH^- \rightarrow P + 2\ H_2O + e^-$$

Therefore, the conducting polymer converts to non-conducting form. In other words, polymer on the electrode surface is unstable. In acidic regions with a pH value below 4, PANI chains contain more dedoped forms such as L species which are non-conducting, and as a result, polymers partially lose their electroactivity. In conclusion, the pH of the medium must be equal to 4.0 for electrocatalytic-purpose use.

Response of Composite Coating to Catechol and Hydroquinone

The responses of composite, PANI coatings to catechol and hydroquinone in phenolic compounds were investigated at pH 4 in $NaHSO_4/Na_2SO_4$ solution. Chronocoulometric curves of the coated electrodes at various potentials between 0.40 and 0.90 V were taken in $NaHSO_4/Na_2SO_4$ solutions containing 5.00 mM catechol and 5.00 mM hydroquinone and then the amount of charge was measured after 1200 s. Figure 12 shows the graph of

charge plotted versus applied potential of bulk electrolysis. Table II summarizes the results obtained in the presence and absence of these phenolic species. This experiment was not performed for $PVF^{+}ClO_4^{-}$ due to the removal of film from the Pt surface during bulk electrolysis. As shown in Table II, in the presence of catechol and hydroquinone, the oxidation potential in which maximum charge was obtained for PANI film shifted from 0.65 to 0.60 V, while it shifted from 0.60 to 0.55 V for composite film. In other words, the oxidation potential was shifted to more negative values. More-

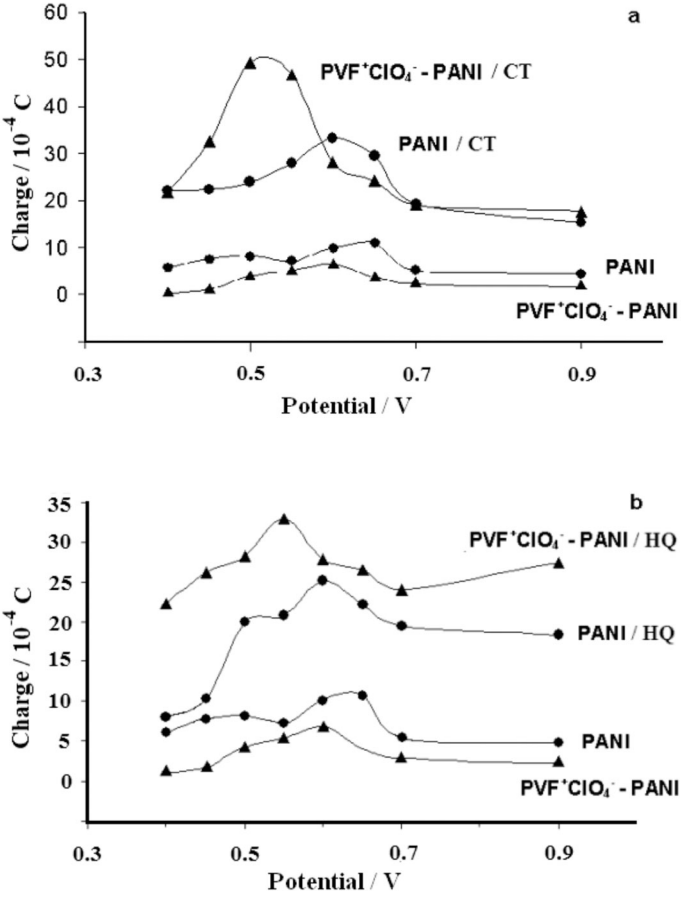

FIG. 12

Plot of the charge amount after electrolysis of 1200 s in $NaHSO_4/Na_2SO_4$ solution (pH 4.0) containing 5.0 mM a catechol and b hydroquinone for PANI and $PVF^{+}ClO_4^{-}$-PANI films versus the applied potential in bulk electrolysis

over, the amount of charge also increased significantly. The amount of maximum charge for PANI and $PVF^+ClO_4^-$-PANI composite films increased approximately 3.1 and 7.5 times in the presence of catechol, respectively. Also, the amount of maximum charge for these films increased approximately 2.3 and 5.0 times in the presence of hydroquinone, respectively. In conclusion, the catalytic activity of PANI polymer was improved by the addition of $PVF^+ClO_4^-$ polymer. The most significant contribution of $PVF^+ClO_4^-$ to the composite film is its facilitation of electron transfer. It could be concluded that determination of phenolic species such as catechol and hydroquinone on composite coated electrode is possible at more negative potentials with much more enhanced current values without using any enzyme.

TABLE II
Maximum amount of charge for PANI and $PVF^+ClO_4^-$-PANI coated electrode after electrolysis of 1200 s in $NaHSO_4/Na_2SO_4$ buffer solutions (pH 4.0) containing 5.0 mM catechol, 5.0 mM hydroquinone and their applied potential values in the bulk electrolysis

Phenolic species	PANI		$PVF^+ClO_4^-$-PANI	
	E, V	Q_{max}, C	*E*, V	Q_{max}, C
–	0.65	1.07×10^{-3}	0.60	6.52×10^{-4}
5.00 mM Catechol	0.60	3.31×10^{-3}	0.55	4.92×10^{-3}
5.00 mM Hydroquinone	0.60	2.51×10^{-3}	0.55	3.29×10^{-3}

CONCLUSIONS

To combine the electrocatalytic properties of a redox polymer and an intrinsically conducting polymer, electrosynthesis of $PVF^+ClO_4^-$-PANI composite film has been performed on Pt electrode in non-aqueous medium for the first time. When the composite film was prepared by cycling the potential between 0.20 and 1.80 V vs Ag|AgCl in a methylene chloride solution containing a mixture of PVF polymer and aniline monomer; $PVF^+ClO_4^-$ and PANI polymers were codeposited on the electrode surface and hence encapsulated within each other as a mixture. This encapsulation provided the retainment of $PVF^+ClO_4^-$ polymer on the electrode surface even if the polymer was in dedoped form (PVF). This composite coated electrode showed an electrocatalytic effect in the oxidations of catechol and hydroquinone. The role of PVF polymer in composite film is an electron transfer

mediator in the electrochemical oxidation of compounds due to its perfect reversible redox properties. The role of PANI polymer in composite film can form the strong hydrogen bond with phenolic compound. As a result, $PVF^{+}ClO_4^{-}$-PANI composite film prepared in methylene chloride medium is expected to exhibit a promising electrocatalytic effect toward some species, especially phenolic compounds. This catalytic effect may have many advantages in electrochemical determination of some species in both anodic and cathodic regions.

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