



Electropolymerized poly(2-vinylpyridine) coatings as ion-exchange polymer modified electrodes

N. TANTAVICHET, M.D. PRITZKER* and C.M. BURNS

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

(*author for correspondence)

Received 8 March 2000; accepted in revised form 9 September 2000

Key words: electropolymerization, ion-exchange polymer modified electrode, poly(2-vinylpyridine)

Abstract

The effects of pH and of the nature and concentration of the electrolyte on the electrochemical behaviour of the $\text{Fe}(\text{CN})_6^{3-/4-}$ charge-transfer reaction at a poly(2-vinylpyridine)-coated electrode formed by electropolymerization have been studied. Cyclic voltammetry during the $\text{Fe}(\text{CN})_6^{3-}$ incorporation process was combined with measurement of the saturated concentration of the $\text{Fe}(\text{CN})_6^{3-}$ confined in the films to investigate the electrochemical behaviour and the fundamental nature of the ion-exchange polymers. The poly(2-vinylpyridine) films formed by electropolymerization were found to have better properties (i.e., larger amount of $\text{Fe}(\text{CN})_6^{3-}$ can be incorporated at various pH values and films are more chemically stable under acidic conditions) as polymer-modified electrodes than those formed by solvent evaporation. Of the various anions studied, ClO_4^- was found to be distinct from the others (Cl^- , NO_3^- , Br^- and SO_4^{2-}). On the one hand, the polymer films exposed to ClO_4^- are more dense and rigid than those exposed to other anions and show relatively little electroactivity. On the other hand, when the films are exposed to increasing concentrations of Cl^- , the films become more swollen, thereby reducing the resistance within the film and enhancing the rate of charge-transfer from the outer film surface to the electrode surface.

1. Introduction

Polymer-modified electrodes have been of great interest for the last two decades. In general, polymer-modified electrodes are composed of redox-active centres confined in thin polymer films and can be classified into two main categories. Fixed-site redox polymers comprising the first category contain redox-active sites covalently attached to an inactive polymeric matrix. Charge transfer in such a polymer film occurs via electron hopping between neighbouring redox-active sites. In the second category are ion-exchange polymers in which redox-active groups are electrostatically bound to the polymer matrix. Since these redox-active species are mobile in the polymer film, the charge transfer across the polymer matrix can occur via physical diffusion of the incorporated redox-active species [1, 2] or via a combination of short-length diffusion and electron hopping of incorporated redox-active species [3].

Usually ion-exchange polymers are formed by solvent evaporation to produce a film followed by incorporation of metal complexes by ion exchange with exchangeable ions. Furthermore, poly(4-vinylpyridine) and its copolymer films rather than poly(2-vinylpyridine) have reportedly been used as polymer-modified electrodes and most have been formed by solvent evaporation, although recently Li and Wang [4] used an electropolymerized

poly(4-vinylpyridine)-modified electrode for the electrocatalyzed oxidation of hydrazine. However, several recent studies have shown that poly(2-vinylpyridine) coatings formed by electropolymerization have some different and advantageous properties (excellent adhesion, hardness, chemical stability and corrosion resistance) over poly(2-vinylpyridine) coatings formed by nonelectrochemical methods [5–7]. This appears to be linked to the fact that electropolymerization leads to a different polymer structure, one with a high degree of crosslinking and branching. Based on these results, it would be important to determine whether such a difference in structure would enable these coatings to be useful for other applications. In the current study, we examine the use of electropolymerization to produce a polymer-modified electrode of poly(2-vinylpyridine) on a graphite substrate and compare this to the use of solvent evaporation. Particular attention will be focused on the influence the method of film formation has on electroactivity and chemical stability of the resulting polymer-modified electrode. One of the disadvantages of ion-exchange polymer-modified electrodes is the potential leakage of redox-active species from the film, leading to a permanent loss of electroactivity. An important objective of this study will therefore be to determine whether the crosslinked and branched nature of the electropolymerized poly(2-vinylpyridine) will help minimize this leakage.

More specifically, the objectives of this research are to electrostatically incorporate a redox-active species, $\text{Fe}(\text{CN})_6^{3-}$, into electropolymerized poly(2-vinylpyridine) films to produce polymer-modified electrodes and to investigate the factors affecting the electrochemical behaviour of these polymer-modified electrodes. This paper will focus on the effects of pH and electrolyte on electropolymerized poly(2-vinylpyridine) films during $\text{Fe}(\text{CN})_6^{3-}$ incorporation by monitoring the cyclic voltammograms obtained during this process and the amount of $\text{Fe}(\text{CN})_6^{3-}$ electrostatically bound in the polymer films. An important factor in the choice of using the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox couple in the polymer-modified electrode is that it has been widely studied in other systems. This should facilitate our ability to distinguish the effects of the nature of the polymer and the method of polymer film formation.

It is expected that pH would have a significant effect on the electroactivity of poly(2-vinylpyridine). Poly(4-vinylpyridine) reportedly can electrostatically bind anionic metal complexes at pH below its $\text{p}K_a$ value (around pH 3) [8] or when it is quaternized by methyl or benzyl halide [9], thereby making it electroactive. Oyama and coworkers [10–12] formed electropolymerized coatings of *N,N*-dialkyl substituted aniline derivatives that could incorporate the same amount of $\text{Fe}(\text{CN})_6^{3-}$ regardless of pH from 1 to 12 and so remain electroactive due to the presence of the strongly basic quaternary ammonium sites. Since no information has been reported on the use of electropolymerized poly(2-vinylpyridine) films as ion-exchange polymers, the dependence of electrochemical behaviour for poly(2-vinylpyridine) films formed by electropolymerization on solution pH will be studied. Comparisons will be made with poly(2-vinylpyridine) films formed by solvent evaporation.

The dependence of the electrochemical behaviour of electropolymerized poly(2-vinylpyridine) on both the nature and concentration of the ionic species comprising the electrolyte is also investigated. Although there have been studies on the effect of the nature of the electrolyte

on ion-exchange polymers [3, 13], very little has been reported on the effect of the electrolyte concentration.

2. Experimental details

2.1. Materials and experimental set-up

2-Vinylpyridine (Sigma-Aldrich Chemical Company) was purified by distillation at 70 °C under vacuum (97.8 kPa) to remove the inhibitor (0.1 wt % *p*-tert-butylcatechol) [5]. All other materials were analytical grade and used as received. Potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$) was purchased from Fisher Scientific. Distilled water was used to prepare solutions in all experiments. Graphite rods (Speer Canada) with diameters of 0.47 cm were used as the working electrodes. They were washed with deionized water and dried in an oven before weighing and beginning the electropolymerization process.

The electrochemical processes to form the poly(2-vinylpyridine) coating and then incorporate $\text{Fe}(\text{CN})_6^{3-}$ were controlled by a potentiostat/galvanostat (EG&G Princeton Applied Research, model 273) using a three-electrode electrochemical cell with a platinum counter electrode and a standard calomel reference electrode (SCE, Fisher Scientific). The working electrode (poly(2-vinylpyridine)-coated graphite) was placed in the middle of the electrolytic cell surrounded by a platinum coil along the internal wall of the cell, as shown in Figure 1. The current data were recorded as a function of time with a personal computer. All reported potentials refer to the SCE scale. The electrolytic solution was well agitated by a magnetic stirrer throughout the experiments.

2.2. Film formation

The electropolymerization procedure to form poly(2-vinylpyridine) films followed the method reported by Ling et al. [5]. The aqueous electrolytic solution was

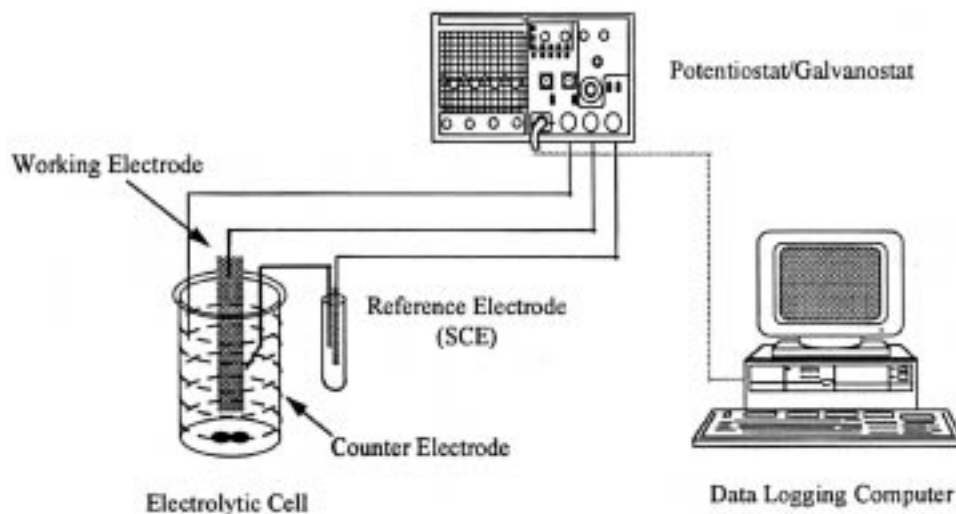


Fig. 1. Equipment set-up for incorporation of the metal complex into the electropolymerized poly(2-vinylpyridine) coated electrode.

prepared to contain 0.25 M 2-vinylpyridine, 0.05 M NH_4ClO_4 and 20 vol % methanol. The pH of the solution was then adjusted from about 7.4 to 4.85 with concentrated HClO_4 . The exposed area of the graphite rod in the solution was 4.66 cm^2 (0.476 cm in diameter and 3.0 cm in length). Electropolymerization of the poly(2-vinylpyridine) was carried out by applying three consecutive cyclic voltammetric scans between -0.7 and -2.5 V at 30 mV s^{-1} . The mass of the polymer coating controlled by the number of cycles or the electropolymerization time, was obtained from the weight increase of the graphite rod after electropolymerization. The typical mass of the polymer film obtained after three cycles of voltammetry was found to be approximately 4.7 mg. Using a density of the swollen polymer film to be 0.9 g cm^{-3} based on the average values of the bulk density of polyvinylpyridine (1.1 g cm^{-3}) [14] and the approximated density of swollen poly(4-vinylpyridine) film formed by solvent evaporation (0.65 g cm^{-3}) [15], this corresponds to a thickness of about $11.1 \mu\text{m}$.

Poly(2-vinylpyridine) films were also formed on the graphite electrode by solvent evaporation for comparison purposes. This involved first forming a bulk poly(2-vinylpyridine) solution by free radical polymerization initiated by 1.0 wt % benzoyl peroxide (Sigma-Aldrich) at room temperature ($20 \text{ }^\circ\text{C}$). The polymer was isolated by hexane. A graphite rod was then dipped in the solution of poly(2-vinylpyridine)/methanol to form the polymer coating on the surface. More details of the procedure are given by Ling et al. [6].

2.3. Incorporation of $\text{Fe}(\text{CN})_6^{3-}$

Under typical conditions, $\text{Fe}(\text{CN})_6^{3-}$ was incorporated into the poly(2-vinylpyridine) film by cyclic voltammetric electrolysis in a $0.002 \text{ M K}_3\text{Fe}(\text{CN})_6$ and 0.5 M KCl aqueous solution at pH 3 adjusted with HCl . The potential of a poly(2-vinylpyridine)-coated electrode was cyclically scanned between $+0.5$ and -0.2 V at 50 mV s^{-1} for 30 min to incorporate $\text{Fe}(\text{CN})_6^{3-}$ into the film. This technique not only enables the incorporation of $\text{Fe}(\text{CN})_6^{3-}$ into the polymer films to take place but also provides dynamic information concerning the process itself.

2.4. Measurement of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ incorporated in films

Although cyclic voltammetry was used to incorporate $\text{Fe}(\text{CN})_6^{3-}$ in the films, determination of the area under the voltammetric curves tended to underestimate the amount incorporated into the coating. Thus, in this study, the method originally presented by Oyama and Anson [16] was used to estimate the amount of $\text{Fe}(\text{CN})_6^{3-}$ incorporated into the coating. After the incorporation process, the polymer-coated electrode was transferred to a solution containing 0.5 M KCl , but no ferri- or ferrocyanide, at the same pH as during the incorporation process to determine the amount

(Γ ; in mol cm^{-2}) of $\text{Fe}(\text{CN})_6^{3-}$ incorporated into the coating. The potential of the polymer-coated electrode was then adjusted from its open-circuit value ($\sim 0.22 \text{ V}$) to $+0.50 \text{ V}$, then scanned at 50 mV s^{-1} from $+0.5$ to -0.2 V and then held at -0.2 V until the current decreased to the background level to ensure that all $\text{Fe}(\text{CN})_6^{3-}$ is converted to $\text{Fe}(\text{CN})_6^{4-}$. The amount of $\text{Fe}(\text{CN})_6^{3-}$ in the film was estimated by measuring the area under the reduction current curve obtained while the electrode potential was scanned from $+0.5$ to -0.2 V and then held at -0.2 V . The concentration (c_f^0 ; in mol cm^{-3}) of $\text{Fe}(\text{CN})_6^{3-}$ incorporated in the polymer film was determined from the Γ value by using the estimated thickness (ϕ) of the swollen film, that is, $c_f^0 = \Gamma/\phi$.

The amount of $\text{Fe}(\text{CN})_6^{4-}$ incorporated in the film was measured in a similar way to that described above. Once the incorporation process was complete, the electrode was transferred to a solution containing 0.5 M KCl , but no ferri- or ferrocyanide, at the same pH as during incorporation. The electrode potential was stepped to -0.2 V , then scanned at 50 mV s^{-1} from -0.2 to 0.5 V and then held at 0.5 V until the current decreased to the background level. The amount of $\text{Fe}(\text{CN})_6^{4-}$ in the film was estimated by measuring the area under the oxidation current curve as the potential was scanned from -0.2 to 0.5 V and then held at 0.5 V .

3. Experimental results and discussion

3.1. Effect of solution pH on the incorporation of $\text{Fe}(\text{CN})_6^{3-}$ into electropolymerized films

A series of cyclic voltammograms obtained during the incorporation of $\text{Fe}(\text{CN})_6^{3-}$ into the electropolymerized poly(2-vinylpyridine) films in a solution containing $0.002 \text{ M K}_3\text{Fe}(\text{CN})_6$ and 0.5 M KCl at various pH is shown in Figure 2. From the voltammograms at pH 3 (Figure 2(a)), it is observed that the peak current (I_p) on electropolymerized poly(2-vinylpyridine)-coated electrode during the first cycle is somewhat higher than that on an uncoated electrode (Figure 2(e)). Oyama and coworkers [8, 17] obtained similar results with protonated poly(4-vinylpyridine) films formed by solvent evaporation, but their initial peak current on the coated electrode was smaller than that on the uncoated electrode. The voltammograms show a gradual increase in the peak current with successive cycles until it reaches a constant level after 15–20 min at a significantly higher value than that on an uncoated electrode. The leveling off of the current indicates that the polymer film has become saturated with $\text{Fe}(\text{CN})_6^{3-}$.

Using the technique described in Section 2.4, we found the maximum amount of $\text{Fe}(\text{CN})_6^{3-}$ incorporated in the polymer film to be $4.31 \times 10^{-7} \text{ mol cm}^{-2}$ corresponding to a concentration of 0.389 mol L^{-1} (based on an assumed coating density of 0.9 g cm^{-3}). However, analysis showed that the maximum amount of

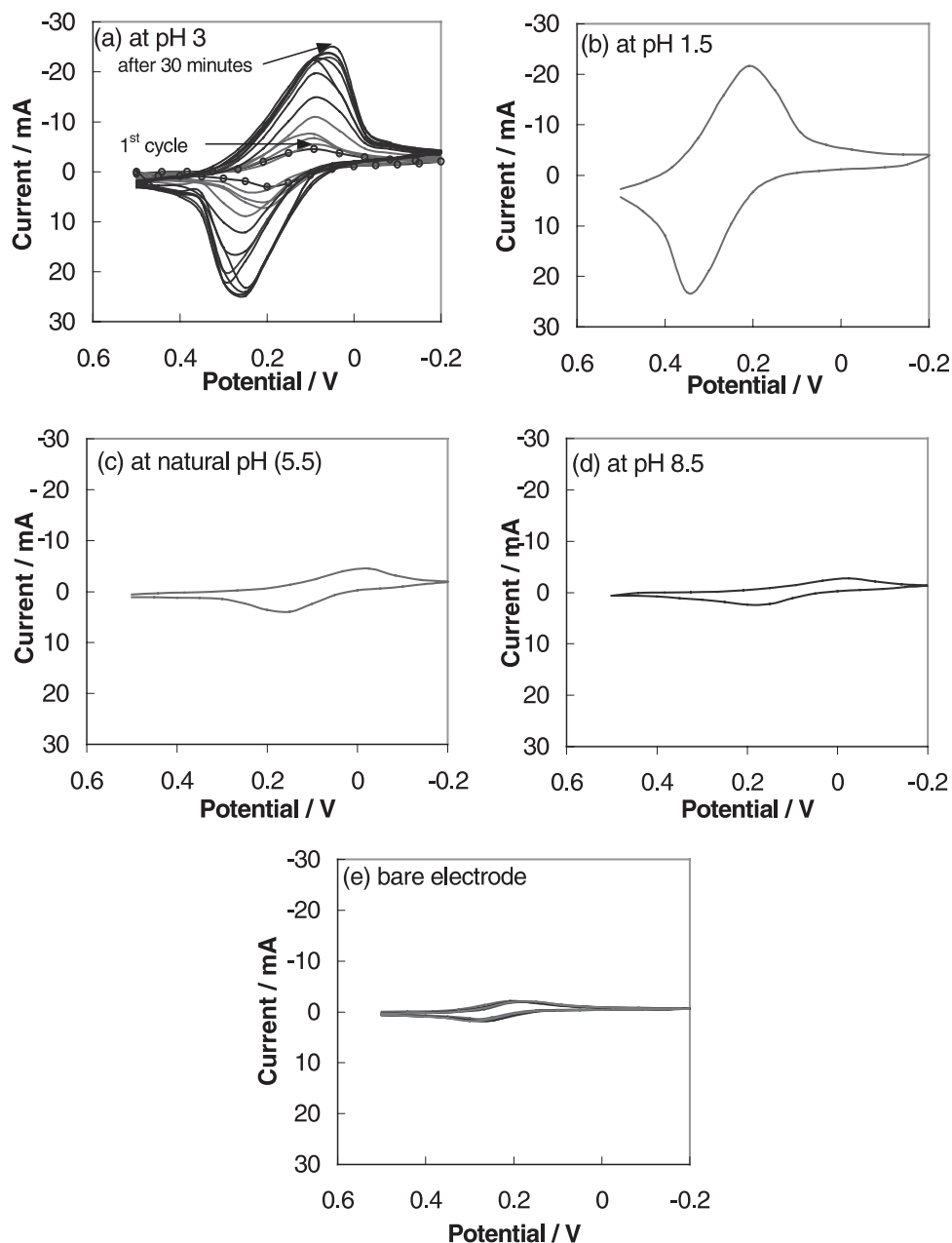


Fig. 2. (a)–(d) Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ on electropolymerized poly(2-vinylpyridine) coated graphite in a solution containing 0.002 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.5 M KCl, with pH adjusted with HCl or KOH. (e) Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ on an uncoated electrode in a solution containing 0.002 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.5 M KCl. The voltammograms show the response at the end of scanning at 50 mV s^{-1} for 30 min.

$\text{Fe}(\text{CN})_6^{4-}$ incorporated was $2.2 \times 10^{-7} \text{ mol cm}^{-2}$. On the basis of electroneutrality, one would expect $3.23 \times 10^{-7} \text{ mol cm}^{-2}$ to be present if every protonated site bound to an $\text{Fe}(\text{CN})_6^{3-}$ ion became bound to an $\text{Fe}(\text{CN})_6^{4-}$ upon reduction. The considerably lower amount of $\text{Fe}(\text{CN})_6^{4-}$ incorporated in the polymer film indicates that the affinity of $\text{Fe}(\text{CN})_6^{4-}$ in the polymer matrix is lower than that of $\text{Fe}(\text{CN})_6^{3-}$, consistent with what has been previously found [13]. This is also consistent with previous findings that electroneutrality requirements tend to drive $\text{Fe}(\text{CN})_6^{4-}$ from the film as reduction of $\text{Fe}(\text{CN})_6^{3-}$ to $\text{Fe}(\text{CN})_6^{4-}$ occurs. This will likely lead to some permanent loss of electroactivity

of the polymer film upon repeated potential cycling unless the bulk solution always contains $\text{Fe}(\text{CN})_6^{3-}$ to replenish the leakage from the film. In this regard, the use of electropolymerization to form the poly(2-vinylpyridine) coatings does not eliminate the problem of leakage of the redox-active species that has also been observed with solvent-evaporated films.

A series of voltammetry experiments were carried out to determine the effect of sweep rate (ν) in solutions containing 0.002 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.5 M KCl at pH 3.0. The peak current for $\text{Fe}(\text{CN})_6^{3-}$ reduction was found to be proportional to the square root of sweep rate suggesting that the charge transfer is controlled by

diffusion through the polymer film [18]. The linear relationship $I_p/v^{1/2}$ enabled the diffusion coefficient (D_{app}) for charge transfer through the protonated electropolymerized poly(2-vinylpyridine) film to be estimated as $5.8 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The polymer film was still stable at this pH of 3.0 after 30 min of electrolysis. This differs from some results in the literature reported on poly(4-vinylpyridine) showing that films formed by solvent evaporation are unstable in KCl/HCl solutions [9].

When the solution pH is further decreased to more acidic conditions (pH 1.5), the final cathodic peak current (Figure 2(b)) remains the same since the pyridine sites in the poly(2-vinylpyridine) film are saturated with H^+ . However, the amount of $\text{Fe}(\text{CN})_6^{3-}$ incorporated ($3.7 \times 10^{-7} \text{ mol cm}^{-2}$) was found to be less than that at pH 3 because some of the polymer film became unstable and dissolved at the lower pH. This was reflected in a weight loss of the coating and the observation of a slight cloudiness in the solution during electrolysis. Although the peak currents do not change when the solution pH changes from pH 3 to 1.5, a positive shift in the cathodic wave and half-wave potential occurs with the development of a more diffusion-like tail. It is expected that the poly(2-vinylpyridine) structure is swollen more at pH 1.5 than at pH 3.0 and $\text{Fe}(\text{CN})_6^{3-}$ can more easily reach the electrode surface leading to a shift in the reduction peak position toward where it is observed on the uncoated graphite electrode. These observations suggest that physical diffusion of $\text{Fe}(\text{CN})_6^{3-}$ is a significant mode of charge transfer within the polymer film.

When no HCl is added to the solution and the pH is at its natural value (pH 5.5), the cathodic peak current (Figure 2(c)) and the amount of $\text{Fe}(\text{CN})_6^{3-}$ incorporated in the polymer film ($1 \times 10^{-7} \text{ mol cm}^{-2}$) not surprisingly are lower than at lower pH, but still higher than that obtained on the bare graphite in the same solution. This

indicates that the electropolymerized poly(2-vinylpyridine) film apparently contains enough protonated sites at pH 5.5 to bind some $\text{Fe}(\text{CN})_6^{3-}$ leading to moderate electroactivity. One possible explanation is that the formation of the coating itself via electropolymerization is conducted in NH_4ClO_4 solution under acidic condition and so H^+ , NH_4^+ and ClO_4^- are incorporated in the film. This argument is supported by evidence from FTIR spectra of electropolymerized poly(2-vinylpyridine) obtained by Ling et al. [6] which show the absorption peak of ClO_4^- . Thus, when this film is contacted with a $\text{Fe}(\text{CN})_6^{3-}$ solution at pH 5.5, exchange with ClO_4^- may allow enough $\text{Fe}(\text{CN})_6^{3-}$ to be incorporated into the coating to lead to a larger reduction current than that observed on a bare electrode.

When the solution pH is basic (pH 8.5), the cathodic peak current (Figure 2(d)) is suppressed and lower than that on the bare electrode, as expected, due to the scarcity of positively charged species in the film (i.e., no protonation, instability of NH_4^+) to retain $\text{Fe}(\text{CN})_6^{3-}$. In this state, the polymer film is electroinactive and serves as a barrier to inhibit the transport of $\text{Fe}(\text{CN})_6^{3-}$ through the polymer film.

The effect of pH on the amount of $\text{Fe}(\text{CN})_6^{3-}$ incorporated in the films is shown in Figure 3. As the solution pH decreases from the natural solution pH of 5.5, the amount of $\text{Fe}(\text{CN})_6^{3-}$ bound in the poly(2-vinylpyridine) films increases steeply and reaches a maximum at pH between 3.3 and 2.8 before starting to drop off at still lower pH. The amount of $\text{Fe}(\text{CN})_6^{3-}$ confined in the polymer films is found to decrease at pH below 2.75 presumably because the polymer film becomes unstable, as mentioned above. The results suggest that the optimum pH in order to incorporate $\text{Fe}(\text{CN})_6^{3-}$ in the poly(2-vinylpyridine) film is in the range between pH 3.3 and 2.8. A higher pH in this range is preferable since the solution conditions are less severe and the

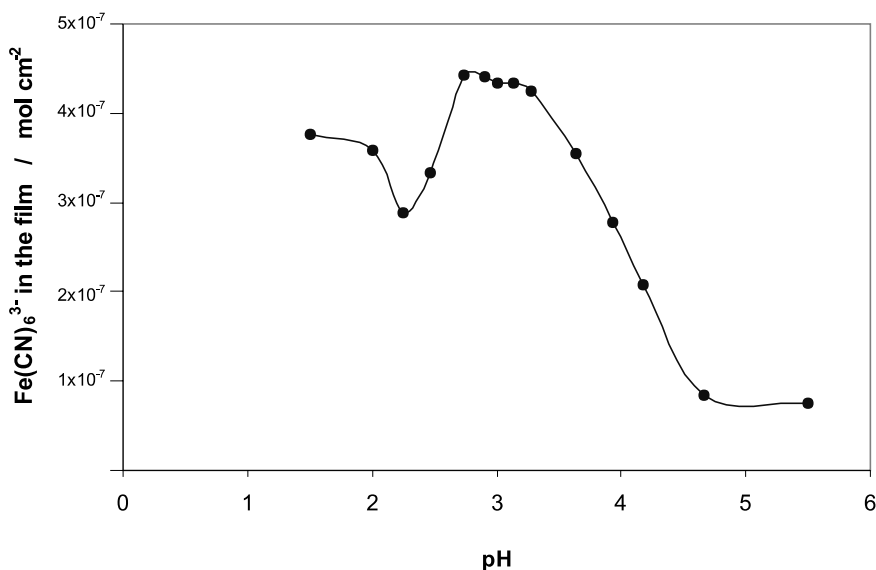


Fig. 3. The amount of $\text{Fe}(\text{CN})_6^{3-}$ incorporated in the electropolymerized poly(2-vinylpyridine) coating on the graphite electrode as a function of pH after scanning the potential between 0.5 and -0.2 V at 50 mV s^{-1} for 30 min in a solution containing $0.002 \text{ M K}_3\text{Fe}(\text{CN})_6$ and 0.5 M KCl .

poly(2-vinylpyridine) films are more stable. No previous work on the effect of pH on the loading capacity of poly(2-vinylpyridine) has been reported and only very little has been reported with regard to poly(4-vinylpyridine). Oyama and Anson [8] showed that poly(4-vinylpyridine) is highly protonated at pH below 3 and essentially neutral at higher pH so that these electrodes have to be exposed to acidic electrolyte in order for metal complexes to be incorporated into these films. The dependence on pH of an electropolymerized poly(2-vinylpyridine)-coated electrode studied here is different from that of electropolymerized *N,N*-dialkyl substituted aniline derivative polymer films [10–12] that can incorporate the same amount of $\text{Fe}(\text{CN})_6^{3-}$ independent of pH from 1 to 12 due to the presence of strongly basic quaternary ammonium sites.

3.2. Effect of solution pH on the incorporation of $\text{Fe}(\text{CN})_6^{3-}$ into films formed by solvent evaporation

For comparison, experiments were conducted on poly(2-vinylpyridine) films formed by solvent evaporation under natural (pH 5.5) and acidic (pH 3) conditions to produce the cyclic voltammograms shown in Figures 4 and 5, respectively. Unlike the current response of the electropolymerized-coated electrode (Figure 4(a)), the response of poly(2-vinylpyridine)-coated electrode at pH 5.5 formed by solvent evaporation (Figure 4(b)) is entirely suppressed and even lower than that on an uncoated electrode (Figure 4c). This indicates that the polymer films formed by solvent evaporation are not as electroactive as those formed by electropolymerization at pH 5.5. Previous reports in the literature [9, 14] implied that poly(4-vinylpyridine) coatings formed by solvent evaporation cannot electrostatically bind the metal complexes and thereby significantly inhibit redox reactions unless the films are protonated or quaternized. This behaviour represents a potential advantage for the

use of electropolymerization over solvent evaporation since acidic conditions might be too aggressive for the polymer films. It may be preferable to operate under milder conditions provided the polymer films formed by electropolymerization have sufficient electroactivity.

At pH 3, the observed current through the polymer films formed by solvent evaporation (Figure 5(b)) increases considerably from what is observed at pH 5.5, but is still lower than that through the polymer films formed by electropolymerization. Furthermore, the polymer films formed by solvent evaporation are very unstable at this pH and some actually partially peeled off the electrode surface. The electrolyte changed from clear to very cloudy with fragments of the peeled poly(2-vinylpyridine) film suspended throughout the solution. It is important to note that no such effects were observed with the electropolymerized coatings at this pH. The instability of the poly(vinylpyridine)-modified electrodes in KCl solutions with HCl used to adjust the solution pH has been reported by other researchers [9]. Thus, an electrolytic solution of $\text{CF}_3\text{COONa}/\text{CF}_3\text{COOH}$ has been widely used instead. Figure 6 shows cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ on electropolymerized poly(2-vinylpyridine)-coated and solvent evaporation-coated electrodes in $\text{CF}_3\text{COONa}/\text{CF}_3\text{COOH}$ solution at pH 3. Both types of polymer films are stable under this condition. The results again indicate a larger reduction current when the electropolymerized coating is used. Also, the separation between the reduction and oxidation peaks for $\text{Fe}(\text{CN})_6^{3-/4-}$ on films formed by solvent evaporation is much wider ($\Delta E = 0.495$ V) than that of poly(2-vinylpyridine) films formed by electropolymerization ($\Delta E = 0.231$ V). The peak positions for $\text{Fe}(\text{CN})_6^{3-}$ reduction and $\text{Fe}(\text{CN})_6^{4-}$ oxidation shift to more negative and to more positive potentials, respectively. These trends indicate more resistance to the

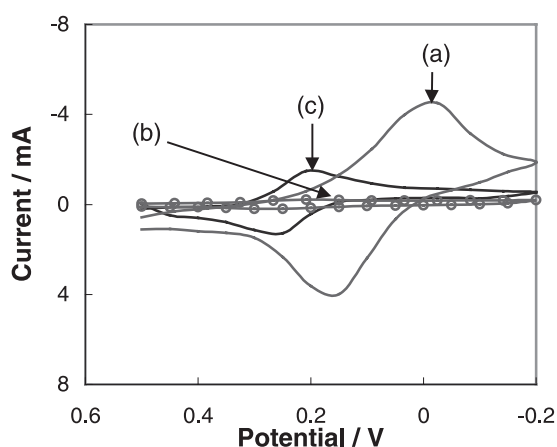


Fig. 4. Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ on various electrodes in a solution containing 0.002 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.5 M KCl at natural pH (5.5): (a) electropolymerized poly(2-vinylpyridine)-coated graphite; (b) graphite coated with poly(2-vinylpyridine) by solvent evaporation; (c) bare graphite. The voltammograms correspond to the responses at the end of scanning between 0.5 and -0.2 V at 50 mV s^{-1} for 30 min.

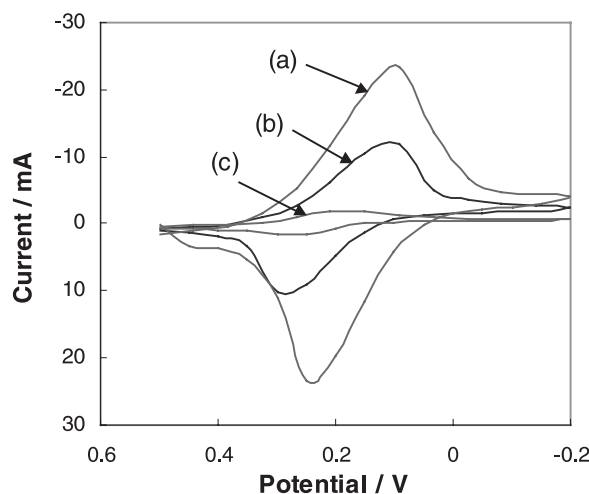


Fig. 5. Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ on various electrodes in a solution containing 0.002 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.5 M KCl at pH 3: (a) electropolymerized poly(2-vinylpyridine)-coated graphite; (b) graphite coated with poly(2-vinylpyridine) by solvent evaporation; (c) bare graphite. The voltammograms correspond to the responses at the end of scanning between 0.5 and -0.2 V at 50 mV s^{-1} for 30 min.

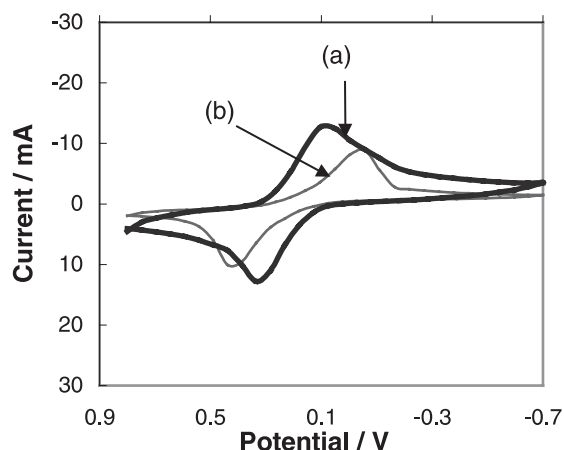


Fig. 6. Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ on various electrodes in solutions containing 0.002 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.2 M CF_3COONa at pH 3: (a) electropolymerized poly(2-vinylpyridine)-coated graphite; (b) graphite coated with poly(2-vinylpyridine) by solvent evaporation. The voltammograms correspond to the responses at the end of scanning between 0.8 and -0.7 V at 50 mV s^{-1} for 30 min.

reaction of $\text{Fe}(\text{CN})_6^{3-/4-}$ on the solvent evaporation-coated electrode in this electrolyte, similar to what is observed in chloride solutions.

These experimental results indicate that the poly(2-vinylpyridine) films formed by electropolymerization may be more suitable for use in polymer-modified electrodes than those formed by solvent evaporation from several perspectives, for example, better electroactive properties (i.e., higher voltammetric current and less film resistance) at both natural and acidic conditions as well as forming more stable coatings under aggressive conditions (i.e., solutions containing KCl and HCl).

3.3. Effect of electrolyte on the incorporation of $\text{Fe}(\text{CN})_6^{3-}$ into the polymer films

In this study, the effects of both the nature and concentration of the electrolyte on the voltammetric current responses and on the amount of $\text{Fe}(\text{CN})_6^{3-}$ confined in the electropolymerized poly(2-vinylpyridine) films have also

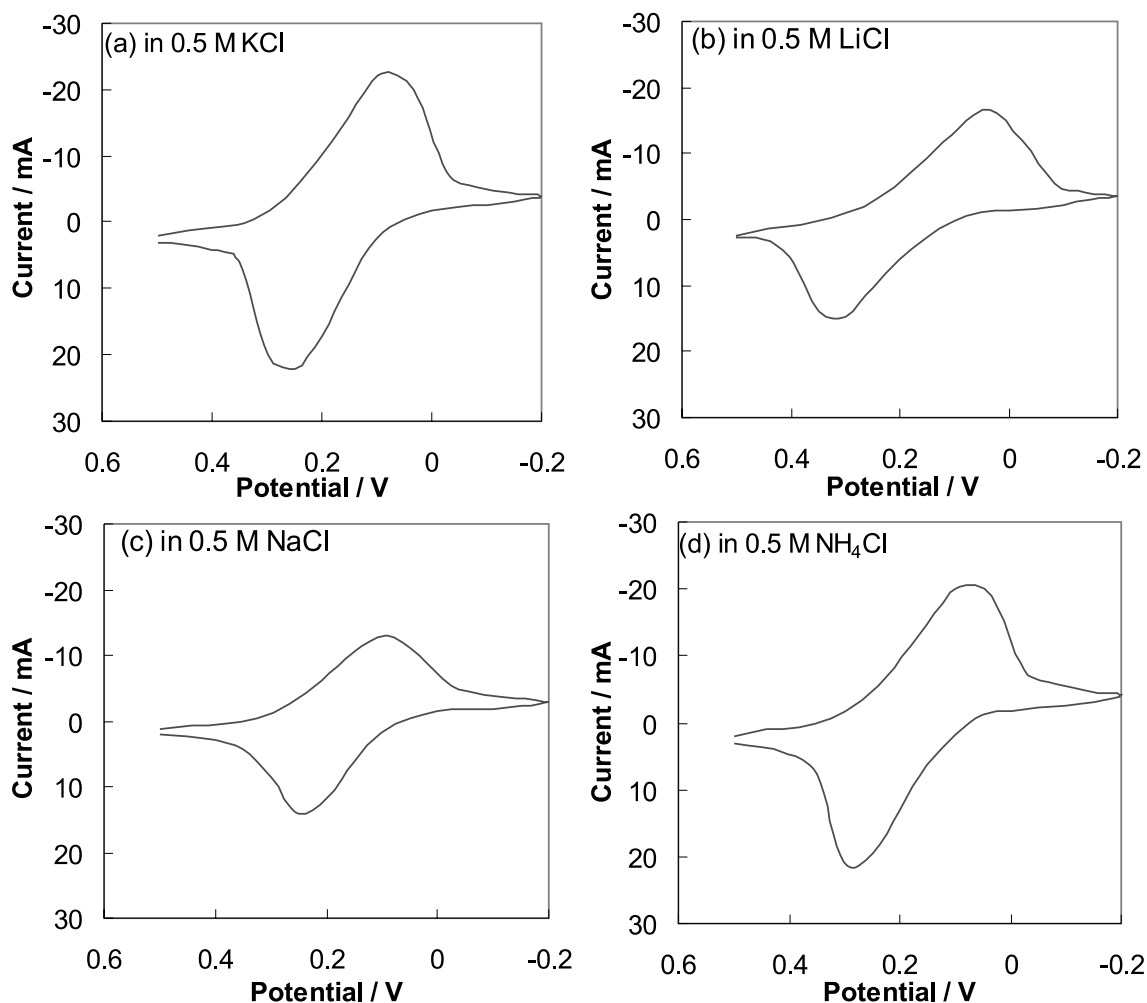


Fig. 7. Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ on electropolymerized poly(2-vinylpyridine) coated graphite in solutions containing 0.002 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.5 M of different electrolytes: (a) KCl; (b) LiCl; (c) NaCl; (d) NH_4Cl ; (e) KNO_3 ; (f) NH_4NO_3 ; (g) KBr; (h) $(\text{NH}_4)_2\text{SO}_4$; (i) NaClO_4 , at pH 3 adjusted with their corresponding acids. All voltammograms correspond to the responses after scanning between 0.5 and -0.2 V at 50 mV s^{-1} for 30 min.

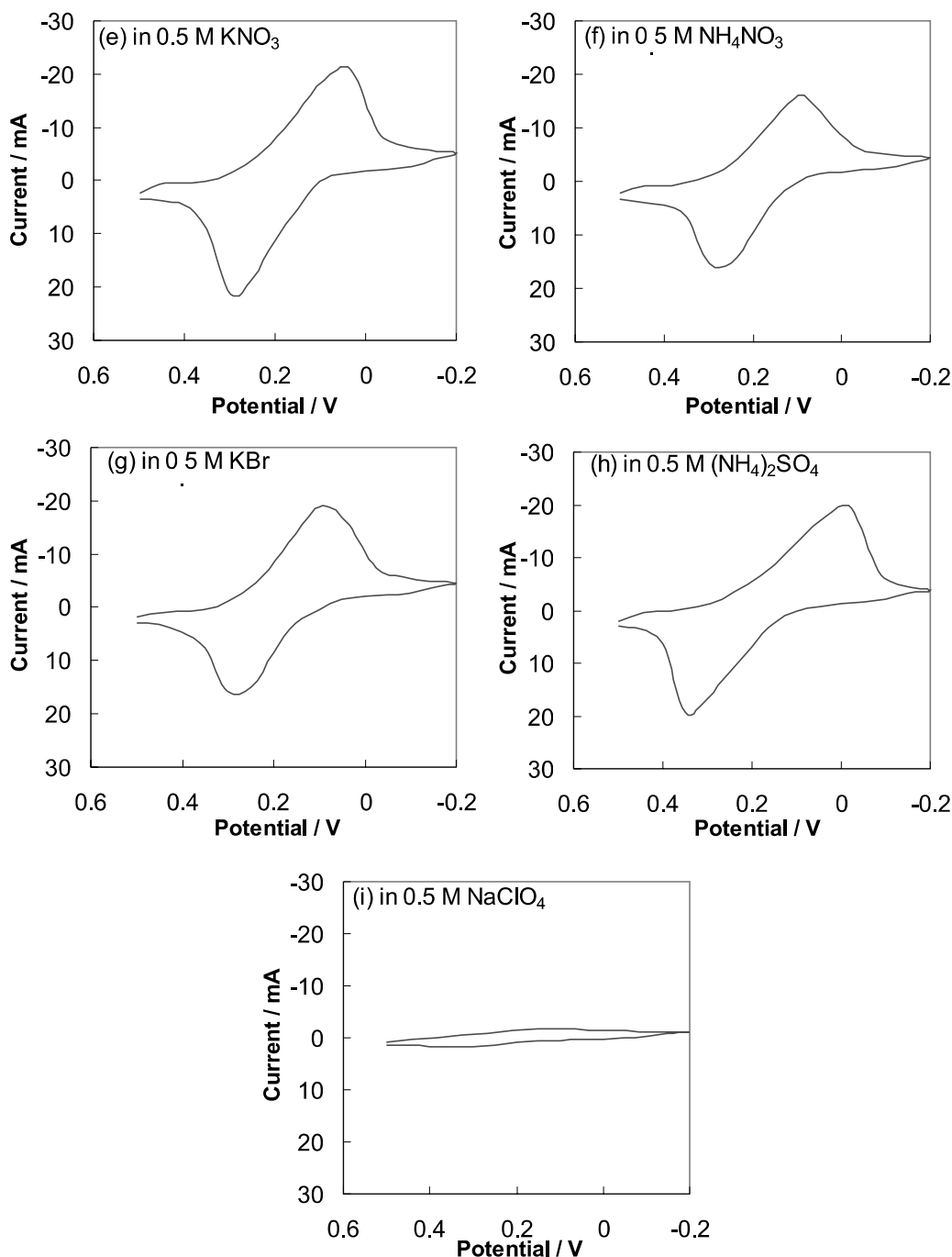


Fig. 7. (Continued)

been investigated. Figure 7 presents the voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ on electropolymerized poly(2-vinylpyridine)-coated electrodes in 0.5 M of different electrolytes KCl, LiCl, NaCl, NH_4Cl , KNO_3 , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, KBr and NaClO_4 at pH 3 after 30 min of scanning. The corresponding amount of $\text{Fe}(\text{CN})_6^{3-}$ incorporated in the polymer films is listed in Table 1. The voltammograms in Figure 7(a) to (d) indicate that the nature of the cation in a chloride electrolyte has some effect on the amount of charge transfer within the polymer films. The currents for $\text{Fe}(\text{CN})_6^{3-}$ reduction and consequently for $\text{Fe}(\text{CN})_6^{4-}$ oxidation on the reverse scan are lower in the presence of Na^+ and Li^+ than K^+ and NH_4^+ .

The nature of the anion is found to have an even larger effect on the electrode responses than that of the cation. Comparison of Figure 7(d), (f) and (h) indicates that the presence of SO_4^{2-} causes a larger separation between the reduction and oxidation peaks. However, the most significant effect is observed upon the addition of ClO_4^- (Figure 7(i)). This leads to a dramatic suppression in the current response by an order of magnitude to a level lower than that observed on bare graphite in 0.5 M KCl solution. This indicates that the polymer film in ClO_4^- solutions behaves as an electroinactive barrier preventing the incorporation of $\text{Fe}(\text{CN})_6^{3-}$ in the polymer film and inhibiting the transport of $\text{Fe}(\text{CN})_6^{3-}$ to the

Table 1. The amount of $\text{Fe}(\text{CN})_6^{3-}$ incorporated in the electropolymerized poly(2-vinylpyridine) films in different solutions, as determined after 30 min of cyclic potential scanning in the experiments in Figure 7

Electrolyte (0.5 M)	Amounts of $\text{Fe}(\text{CN})_6^{3-}$ in polymer films /mol cm ⁻²
KCl	4.31×10^{-7}
LiCl	3.81×10^{-7}
NaCl	3.33×10^{-7}
NH_4Cl	4.39×10^{-7}
KNO_3	2.65×10^{-7}
NH_4NO_3	3.82×10^{-7}
KBr	3.56×10^{-7}
$(\text{NH}_4)_2\text{SO}_4$	2.87×10^{-7}
NaClO_4	2.50×10^{-8}

graphite surface. The maximum amount of $\text{Fe}(\text{CN})_6^{3-}$ confined in the poly(2-vinylpyridine) films in NaClO_4 solution is found to be only 2.5×10^{-8} mol cm⁻², only 6% of that observed in KCl solutions, while the diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-}$ in the film is found to be smaller than that for other electrolytes by two orders of magnitude.

These differences are more reflective of the effect of the anions on the polymer structure than on differences in the rates of anion transfer through the polymer film. The polymer matrix interacts especially strongly with ClO_4^- with the result that crosslinking occurs [19–21], whereas the interactions between the polymer matrix and other anions are much weaker. Thus, the polymer film has a much more rigid and compact internal structure in a ClO_4^- electrolyte, while the polymer films in other electrolytes have a more swollen and open structure. Infrared spectra results by Oh and Faulkner [3] for polymer films in different anionic electrolytes along with Raman spectroscopy results previously reported by Walrafen [22] have shown that the hydrogen-bonded water in polymer films is destroyed in the presence of ClO_4^- causing the polymer films to dehydrate and become more compact.

These results also reflect the relative affinities of the various anions for the protonated polymer matrix. Clearly, $\text{Fe}(\text{CN})_6^{3-}$ has a much higher affinity than Cl^- , NO_3^- , Br^- and SO_4^{2-} considering that its bulk concentration is two orders of magnitude lower than that of the other anions, but still can be incorporated into the film. On the other hand, it is difficult to conclude whether $\text{Fe}(\text{CN})_6^{3-}$ or ClO_4^- has higher affinity on the basis of these results since the ClO_4^- concentration is so much higher than that of $\text{Fe}(\text{CN})_6^{3-}$. It should be noted that Niwa and Doblhofer [13] concluded that ClO_4^- has a higher affinity than $\text{Fe}(\text{CN})_6^{3-}$ for poly(4-vinylpyridine) films on the basis of infrared reflection-absorption spectroscopy results.

The effect of ClO_4^- on the poly(vinylpyridine) structure, as discussed above, is consistent with its effect on the electropolymerization process to form poly(2-vinylpyridine) films on the electrode surface in the first place. As reported in a previous study [5, 21], good quality

coatings (i.e., thick and uniform films with excellent adhesion to the substrate) were obtained only when electropolymerization was conducted in the electrolytes containing ClO_4^- as anions (NH_4ClO_4 , KClO_4 and HClO_4). However, polymer films formed in electrolytes containing other anions (KCl , NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , $(\text{NH}_4)_3\text{PO}_4$ and H_3PO_4) were very thin, relatively loose and powdery. These observations are consistent with the present observation regarding ion-exchange polymers since one would expect better coatings in an electrolyte that promotes dehydration and crosslinking of the polymer segments, leading to a compact, rigid and stable coating. The other anions do not promote significant crosslinking between the polymer segments, thereby yielding only thinner, looser and powdery coatings.

The concentration of KCl was found to affect the structure of polymer films, as shown by cyclic voltammograms in Figure 8. The peak positions are affected by the KCl concentration. The peak separations are wider and the half-wave potentials shift to more negative values as the KCl concentration decreases. These effects suggest that the polymer structure changes with electrolyte concentration. When the concentration of KCl is higher, the polymer structure is more swollen. Thus, the films of poly(2-vinylpyridine) are more open leading to a decrease in the film resistance. As a result, cathodic and anodic peak positions shift closer to the potentials where the reaction of $\text{Fe}(\text{CN})_6^{3-/4-}$ proceeds on bare graphite and the separation between the peaks for reduction and oxidation diminishes.

Analysis of the cyclic voltammograms in Figure 8 using the technique described in Section 2.4 shows that a KCl concentration of 0.5 M produces the highest loading of $\text{Fe}(\text{CN})_6^{3-}$ (Table 2). The amount of $\text{Fe}(\text{CN})_6^{3-}$ confined in the poly(2-vinylpyridine) film and the peak current are found to be lowest at the highest KCl

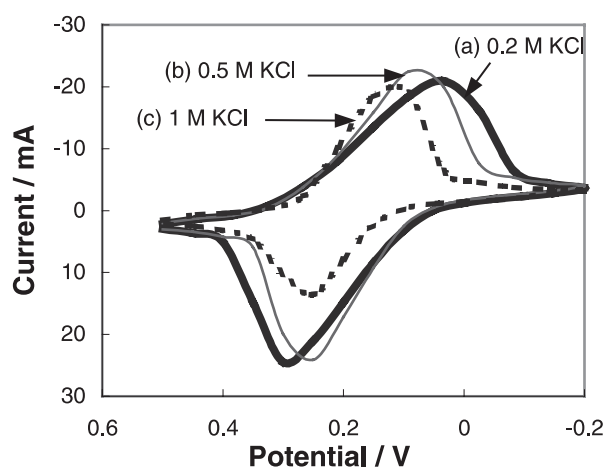


Fig. 8. Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$ on electropolymerized poly(2-vinylpyridine) coated graphite in solutions containing 0.002 M $\text{K}_3\text{Fe}(\text{CN})_6$ and different KCl concentrations: (a) 0.2 M KCl; (b) 0.5 M KCl; (c) 1 M KCl, at pH 3 adjusted with HCl. The voltammograms correspond to the responses at the end of scanning between 0.5 and -0.2 V at 50 mV s^{-1} for 30 min.

concentration (1 M). This effect may be explained by the breakdown of Donnan exclusion of Cl^- ions [13]. At high enough Cl^- concentration in the solution (i.e., 1 M), Cl^- can compete with $\text{Fe}(\text{CN})_6^{3-}$ for the binding sites in the polymer leading to a lowering of the amount of $\text{Fe}(\text{CN})_6^{3-}$ incorporated in the film. The polymer film treated in 0.2 M KCl appears to be more stable than those treated at higher KCl concentrations, although the amount of $\text{Fe}(\text{CN})_6^{3-}$ in the polymer film at this concentration is slightly less than that in 0.5 M KCl. The less swollen polymer structure at 0.2 M KCl allows less $\text{Fe}(\text{CN})_6^{3-}$ to penetrate through the film.

The importance of film stability is demonstrated by the cyclic voltammograms in Figure 9 obtained by immersing poly(2-vinylpyridine)-coated electrodes pre-loaded with $\text{Fe}(\text{CN})_6^{3-}$ in 0.5 M (Figure 9(a)) and 0.2 M (Figure 9(b)) KCl solutions. No $\text{Fe}(\text{CN})_6^{3-}$ is added to the KCl solutions. A significant and rapid decrease in the current response in 0.5 M KCl is observed. After 2 h of electrolysis, the reduction peak current has decreased by 67% of the initial value. In the presence of 0.2 M KCl, on the other hand, the peak current retains its initial value for 30 min and decreases by about 25% after 2 h of electrolysis. This loss in electroactivity is consistent with the conclusion made in Section 3.1 that the conversion of $\text{Fe}(\text{CN})_6^{3-}$ to $\text{Fe}(\text{CN})_6^{4-}$ results in leakage of $\text{Fe}(\text{CN})_6^{4-}$ from the film. With no $\text{Fe}(\text{CN})_6^{3-}$ present in the bulk solution during the experiments presented in Figure 9, this leads to a steady decline in electroactivity as cycling continues. Comparison of the results in Figure 9(a) and (b) indicates that the polymer film is more stable at the lower concentration, but not at the higher concentration in the 2 h electrolysis. With no $\text{Fe}(\text{CN})_6^{3-}$ in the solution to compete with Cl^- , some Cl^- can enter the polymer film and displace $\text{Fe}(\text{CN})_6^{3-}$. The replacement of $\text{Fe}(\text{CN})_6^{3-}$ by Cl^- leads to a more swollen polymer structure, facilitating further diffusion of $\text{Fe}(\text{CN})_6^{3-}$ out of the polymer film. Lower voltammetric currents and ultimate film instability are, therefore, observed. Taken together, these results show that the use of 0.2 M KCl gives the best compromise between incorporating $\text{Fe}(\text{CN})_6^{3-}$ and affording the coating adequate stability. Another contributing factor is that $\text{Fe}(\text{CN})_6^{4-}$ produced during the reduction phase of the cycle that remains in the film has a lower affinity for the polymer matrix than $\text{Fe}(\text{CN})_6^{3-}$ [13] and so can be displaced by Cl^- ions.

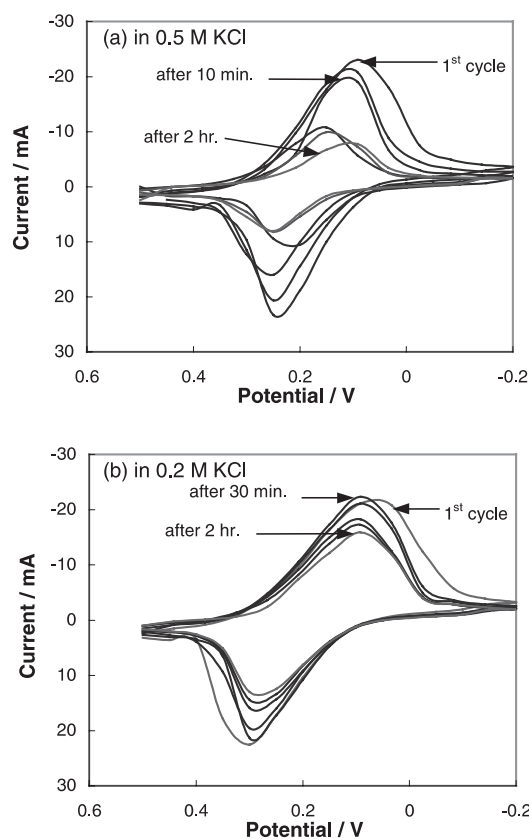


Fig. 9. Cyclic voltammograms of electropolymerized poly(2-vinylpyridine) films previously loaded with $\text{Fe}(\text{CN})_6^{3-}$ in solutions containing (a) 0.5 M KCl, (b) 0.2 M KCl at pH 3. The voltammograms were obtained by scanning between 0.5 and -0.2 V at 50 mV s^{-1} .

4. Conclusions

The poly(2-vinylpyridine) films formed by electropolymerization have been found to have better properties for polymer-modified electrode applications than those formed by solvent evaporation. They have been shown to incorporate more $\text{Fe}(\text{CN})_6^{3-}$ at various values of pH and to be more chemically stable under acidic conditions. This is likely due to the differences in the polymer structure and adhesion to the graphite substrate depending on the method of formation. The variation of the peak potential and peak current with pH and the nature of the anion present in the electrolyte indicate differences in structure resulting from interaction between polymer matrix, ionic species and solvent molecules. As shown previously, ClO_4^- has a distinctive effect on the polymer structure and its presence leads to

Table 2. Effect of KCl concentration on cyclic voltammograms and the incorporation of $\text{Fe}(\text{CN})_6^{3-}$ in electropolymerized poly(2-vinylpyridine) polymer coating on graphite after cyclic potential scanning for 30 min

KCl concentration /M	Peak current, I_p /mA	Half-wave potential /V	Peak separation, ΔE /V	Amount of $\text{Fe}(\text{CN})_6^{3-}$ confined in the coatings /mol cm^{-2}
0.2	21	+0.167	0.267	3.90×10^{-7}
0.5	23	+0.175	0.238	4.31×10^{-7}
1	18	+0.185	0.13	1.87×10^{-7}

the coating becoming electroinactive. Whereas this has been previously found to be useful for purposes of corrosion protection, it is obviously not so for applications of polymer-modified electrodes. In the presence of KCl or other chloride, nitrate, bromide, and sulphate salts and $\text{Fe}(\text{CN})_6^{3-}$, the coating becomes electroactive due to the incorporation of $\text{Fe}(\text{CN})_6^{3-}$ into its structure and the subsequent reduction and oxidation reactions. The amount of salt added is critical in order for the coating to have the optimum properties for charge transfer. If too little salt is present, the polymer structure remains too closed for incorporation and transport of $\text{Fe}(\text{CN})_6^{3-}$; if too much is added, then the structure swells so much that it becomes unstable.

Acknowledgement

The authors express gratitude to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support during this project.

References

1. K. Doblhofer and R. Lang, *J. Electroanal. Chem.* **229** (1987) 239.
2. R. Lang and K. Doblhofer, *J. Electroanal. Chem.* **216** (1987) 241.
3. S.M. Oh and L.R. Faulkner, *J. Electroanal. Chem.* **269** (1989) 77.
4. T. Li and E. Wang, *Electroanalysis* **9** (1997) 1205.
5. X. Ling, J.J. Byerley, M.D. Pritzker and C.M. Burns, *J. App. Electrochem.* **27** (1997) 1343.
6. X. Ling, M.D. Pritzker, J.J. Byerley and C.M. Burns, *Macromolecules* **31** (1998) 9134.
7. I. Sekine, K. Kohara, T. Sugiyama and M. Yuasa, *J. Electrochem. Soc.* **139** (1992) 3090.
8. N. Oyama and F.C. Anson, *J. Electrochem. Soc.* **127** (1980) 247.
9. N. Oyama, T. Shimomura, K. Shigehara and F.C. Anson, *J. Electroanal. Chem.* **112** (1980) 271.
10. N. Oyama, T. Ohsaka and T. Shimizu, *Anal. Chem.* **57** (1985) 1526.
11. T. Ohaka, T. Okajima and N. Oyama, *J. Electroanal. Chem.* **200** (1986) 159.
12. T. Ohaka, T. Okajima and N. Oyama, *J. Electroanal. Chem.* **215** (1986) 191.
13. K. Niwa and K. Doblhofer, *Electrochim. Acta* **31** (1986) 549.
14. N. Oyama and F.C. Anson, *Anal. Chem.* **52** (1980) 1192.
15. N. Oyama, T. Ohsaka and T. Ushirogouchi, *J. Phys. Chem.* **88** (1984) 5274.
16. N. Oyama and F.C. Anson, *J. Electrochem. Soc.* **127** (1980) 640.
17. K. Shigehara, N. Oyama and F.C. Anson, *Inorg. Chem.* **20** (1981) 518.
18. A.J. Bard and L.R. Faulkner, 'Electrochemical Methods. Fundamentals and Applications' (Wiley, New York, 1980), Chapter 5.
19. A.P. Clarke, J.G. Vos, A. Glidle and A.R. Hillman, *J. Chem. Soc. Faraday Trans.* **89** (1993) 1695.
20. D.M. Kelly and J.G. Vos, in M.E.G. Lyons (Ed), 'Electroactive Polymer Electrochemistry, Part 2 Methods and Applications' (Plenum, New York, 1994), chapter 4.
21. X. Ling, M.D. Pritzker, C.M. Burns and J.J. Byerley, *J. Coatings Tech.*, **72**, no. 908 (2000) 71.
22. G.E. Walrafen, *J. Chem. Phys.* **52** (1970) 4190.