Environ. Sci. Technol. **2004**, *38,* 4671−4676

Reduction of Cr(VI) at a Polyaniline Film: Influence of Film Thickness and Oxidation State

SINEAD T. FARRELL AND CARMEL B. BRESLIN*

Department of Chemistry, National University of Ireland Maynooth, Maynooth, County Kildare, Ireland

Hexavalent chromium [Cr(VI)] is highly toxic, carcinogenic, and mutagenic to living organisms. In this paper, the reduction of Cr(VI) to the much less toxic trivalent state [Cr(III)] was studied at polyaniline films grown to different thickness. Much higher rates of Cr(VI) reduction were observed for the "thick" polyaniline films. This was explained in terms of the morphology of the polymer and the higher surface area of polymer in contact with the Cr(VI) solution. For "thin" polyaniline films, the Cr(VI) reduction reaction was found to obey pseudo-first-order kinetics for the duration of exposure. However, in the case of thick polyaniline layers, the Cr(VI) reduction reaction followed a two-stage process, with each stage obeying pseudo-first-order kinetics. This was explained in terms of oxidation of the polymer from the leucoemeraldine to the emeraldine state and then further oxidation of the polymer from the emeraldine to the pernigraniline state. Much higher rates of Cr(VI) reduction were observed on oxidation of the polymer from the leucoemeraldine to the emeraldine state.

Introduction

In recent years there has been considerable interest in the development of procedures for the removal, or reduction, of Cr(VI), which is well-known to be highly toxic, carcinogenic, mutagenic to living organisms, and extremely mobile (*1*). Many of these procedures rely on the reduction of hexavalent chromium to the trivalent state, which is much less toxic and can be easily absorbed into a variety of inorganic and organic materials at neutral pH (*2*). Furthermore, the trivalent chromium can be isolated as insoluble chromium(III) hydroxides by adjusting the pH to sufficiently high values, enabling the removal of chromium from the environment. Many of the current chemical (*3, 4*) and electrochemical treatment (*5, 6*) strategies rely on this reduction step. For example, in the chemical treatments, reducing agents are employed while in the electrochemical treatment direct reduction to the trivalent state is achieved through the application of suitable electrode potentials. However, these processes are not entirely satisfactory; large amounts of secondary waste products, used in the series of treatments, are generated. Consequently, there is a continued need to develop new methods in the remediation of Cr(VI).

* Corresponding author telephone: +353-1-7083677; fax: +353-1-7083815; e-mail: cb.breslin@may.ie.

More recently, it has been shown that conducting polymer films can be used to reduce Cr(VI) (*7*−*12*). The first report of the reduction of hexavalent chromium at a conducting polymer matrix was made by Rajeshwar and co-workers (*7*−*9*), who observed the reduction of hexavalent chromium at a polypyrrole electrode, with approximately 100% efficiency. Furthermore, the reversibility of the polymer redox process enabled the electrochemical recycling of the polypyrrole for repeated treatment of Cr(VI).

Malinauskas and Holze (*13*) have also observed reduction of Cr(VI) at a polyaniline film. Again, the reduction of Cr(VI) was attributed to the oxidation of the polymer. Yang and Hung (*14*), by taking advantage of the electrocatalytic activity of polyaniline, have used a polyaniline/polystyrene composite electrode for the detection and analysis of Cr(VI). Likewise, Mirmohseni and Oladegaragoze (*15*) have fabricated a sensor based on the electrochemical reaction between Cr(VI) and a thin layer of polyaniline, coated at the surface of a quartz crystal electrode. In this latter analysis, a correlation between the mass change and the concentration of Cr(VI) was obtained. Desimoni et al. (*16*) have also reported on a polypyrrole/ferrous−ferric cyanide-coated piezoelectric sensor for Cr(VI).

Although, it is well-known that it is the redox chemistry of polyaniline that enables the reduction of Cr(VI), there is no information available in the literature on the role of the different oxidation states (leucoemeraldine, emeraldine, and pernigraniline) of polyaniline in the Cr(VI) reduction reaction. In this paper, results are presented and discussed on the reduction of Cr(VI) at polyaniline films grown to different thickness. This in turn influences the morphology and redox properties of polyaniline in Cr(VI)-laden solutions, enabling a study on the efficiency of the different oxidation states of polyaniline in the Cr(VI) reduction reaction.

Experimental Section

Electrodes were prepared from pure platinum (99.999+%) rods and platinum wires (99.999+%). The rods were set with epoxy resin in a Teflon holder, and electrical contact was achieved by means of a copper wire attached to the base of the metal sample with conducting silver-loaded resin. Prior to each test, the samples were polished to a smooth surface finish, using successively finer grades of SiC paper, and rinsed with distilled water.

All electrolytes were prepared using analytical grade reagents and distilled water. Prior to use, the aniline was distilled and stored in the dark under an atmosphere of nitrogen. Polyaniline films were electrosynthesized by cycling the platinum electrode in a 0.1 mol dm^{-3} H_2SO_4 solution containing 0.1 mol dm^{-3} aniline, at a scan rate of 50 mV s^{-1}, using a Solartron EI 1287 potentiostat. A standard three-electrode cell was used with a platinum auxiliary electrode and a silver/silver chloride reference electrode.

Reduction of the hexavalent chromium was monitored using a spectrophotometric technique under open-circuit conditions. The polyaniline-coated platinium wire was immersed in a cuvette containing the acidified Cr(VI) solution. A slow stream of nitrogen was passed through the solution to eliminate diffusion interferences. The UV−Vis absorption spectra of the Cr(VI) solution were measured at regular intervals between 200 and 800 nm, using a Cary 50 UV−Vis spectrometer. The concentration of Cr(VI) was calculated from the intense Cr(VI) charge-transfer band centered at 351 nm. In cases where the open-circuit potential was

10.1021/es0498585 CCC: $27.50
Published on Web 07/27/2004

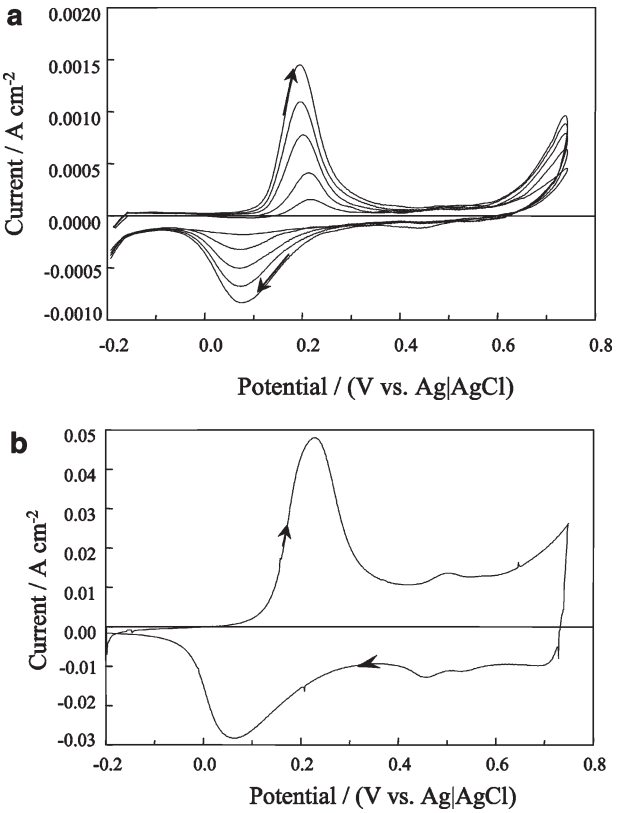


FIGURE 1. (a) Cyclic voltammograms depicting the growth of polyaniline in a 0.1 mol dm^{-3} aniline and 1.0 mol dm^{-3} sulfuric acid solution. 1st, 10th, 20th, 30th, and 40th cycles are shown. (b) Cyclic voltammogram recorded for a "thick" polyaniline film in a 0.1 mol dm^{-3} aniline and 1.0 mol dm^{-3} sulfuric acid solution grown to give a peak current density of 46 $\times$ 10^{-3} A cm^{-2} in the aniline-free solution.

measured during the Cr(VI) reduction reaction, a bare platinum wire was added to the cuvette and used as a reference electrode.

Results and Discussion

Formation of Polyaniline. In Figure 1a, typical data are shown for the electropolymerization of aniline at platinum showing the 1st, 10th, 20th, 30th, and 40th cycles for polarization up to a potential limit of 0.75 V(Ag/AgCl). A preliminary cycle to 0.9 V(Ag/AgCl) was used to initiate radical cation formation, followed by repeated cycling at 50 mV s^{-1} between −0.2 and the lower potential of 0.75 V(Ag/AgCl) to sustain polymer growth without polymer degradation. This procedure, in which oxidation of polyaniline to the higher pernigraniline state was avoided, gave rise to the growth of pure polyaniline layers free from degradation products. It is well-documented in the literature that degradation products, such as benzoquinone, are formed on polarization of the polymer to potentials higher than 0.75 V(Ag/AgCl) (*17*). Consequently, potentials higher than 0.75 V(Ag/AgCl) were not employed in the growth of the polyaniline films. The anodic peak, observed at 200 mV, corresponds to the transition of polyaniline from the poorly conducting leucoemeraldine base/salt to the highly conducting emeraldine state (*18*, *19*) while the corresponding reduction peak is seen at 98 mV. The second redox transition is partially visible at 750 mV and corresponds to the oxidation of polyaniline from the emeraldine to the pernigraniline state. Also, it is interesting to point out that the polyaniline formed using this procedure is relatively free of any degradation products which appear as a "middle peak" between the leucoemeraldine/emeraldine and emeraldine/pernigraniline states (*17*). Such a peak is not observed in Figure 1a. However, when the polymers were grown to peak current values in the region of 50 $\times$ 10^{-3} A, evidence of degradation products could be seen in the voltammograms, as shown in Figure 1b. Here, the benzoquinone/hydroquinone couple can be seen at 0.50 V(Ag/AgCl) in the forward sweep and at 0.45 V(Ag/AgCl) during the reverse sweep. Although, the lower potential limit of 0.75 V(Ag/AgCl) was employed in all cycles following the initial high potential cycle, some degradation of the polymer occurs in this case. This is probably connected with the longer exposure of the deposited polymer to the higher potentials in the vicinity of 0.70−0.75 V(Ag/AgCl), as some hundreds of cycles are required to form these thick polymers.

The thickness of the film grown to a peak current density of 1.5 $\times$ 10^{-3} A (Figure 1a) was estimated as 120 nm using the published relationship of 500 C cm^{-3}, from the measured anodic polyaniline charge obtained from slow sweep cyclic voltammograms recorded in H_2SO_4 between 0.0 and +0.80 V(RHE) (*20*). However, this method is only suitable for estimating the thickness of relatively thin films. Consequently in this study, where the polyaniline films were grown to different thickness, the peak current of the leucoemeraldine/emeraldine redox transition recorded in an aniline-free 0.1 mol dm^{-3} H_2SO_4 solution was taken as an approximate measure of the thickness of the polymers. Throughout the remainder of this paper the term "thin" polyaniline film is used to describe films giving a peak current density of 9 $\times$ 10^{-3} A cm^{-2} in the acidic aniline-free solution, while films grown to give peak current densities higher than 37 $\times$ 10^{-3} A cm^{-2} in the aniline-free solution are denoted as "thick" polyaniline layers.

Reduction of Cr(VI) at Polyaniline. Once these polyaniline layers were formed they were reduced in 0.1 mol dm^{-3} H_2SO_4 at −200 mV (Ag|AgCl) for a 30-min period and then used in the catalysis of the Cr(VI) reduction reaction. It can be seen clearly from Figure 1a that polyaniline resides in the reduced state at −200 mV(Ag/AgCl). Accordingly, the application of this potential for a 30-min period will facilitate the reduction of polyaniline to the fully reduced leucoemeraldine state. The 30-min period is used to ensure reduction of the entire polyaniline film. Typical UV−Vis spectra, showing the uptake of the Cr(VI) at thin and thick polyaniline films are shown in Figure 2 , panels a and b, respectively. The spectra were recorded on immersion of the electrochemically reduced electrodes in acidified 0.25 mmol dm^{-3} Cr(VI) solution at 10-min intervals for a total immersion period of 3 h. The initial spectra after immersion of the thin and thick polymer-coated electrodes are almost identical. In both systems; the charge-transfer band centered at 351 nm for the Cr(VI) complex can be seen clearly. Also, the band featured at 260 nm, which is characteristic of Cr(VI), is seen. The absorbance at these λ_{max} wavelengths decreases with increasing exposure time at both polyaniline electrodes, indicating Cr(VI) reduction. The absorbance values at 351 nm are plotted as a function of the immersion time in the insets of Figure 2a,b and again clearly show a decrease in the Cr(VI) concentrations with increasing immersion time. This reduction of Cr(VI) at the polyaniline electrode can be described by

$$2HCrO_4^-(aq) + 14H^+ + 3Pani^0(s) \rightarrow 2Cr^{3+}(aq) + 3Pani^{2+}(s) + 8H_2O(l) \quad (1)$$

where $Pani^0$ refers to polyaniline in the leucoemeraldine state and $Pani^{2+}$ refers to polyaniline in the emeraldine state. This

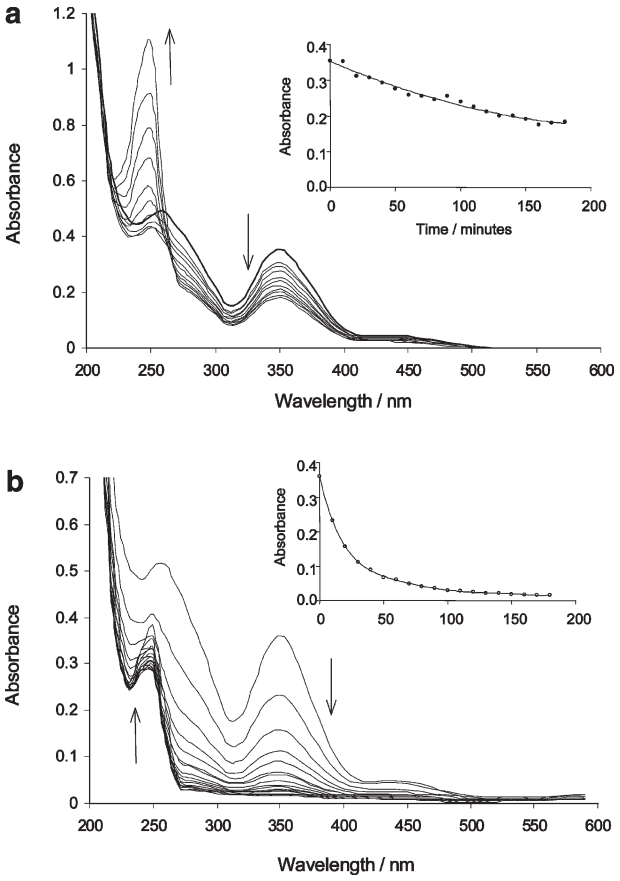
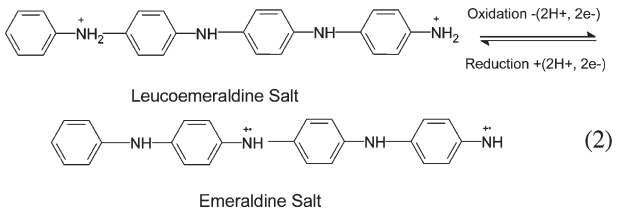


FIGURE 2. UV−Vis spectra of 0.125 mmol dm^{-3} $Na_2Cr_2O_7$ in 0.1 mol dm^{-3} H_2SO_4 during exposure to (a) "thin" (9×10^{-3} A cm^{-2}) and (b) "thick" (71×10^{-3} A cm^{-2}) polymers. Inset gives absorbance at 351 nm as a function of exposure time.

change in the redox state of the polyaniline can be viewed as a two-electron exchange reaction, as shown by



(2)

Evidence for the presence of the trivalent chromium species was obtained on adjusting the pH of the solution using sodium hydroxide. A white precipitate was observed to form, which indicates the presence of Cr(III) and the formation of the $Cr(OH)_3$ precipitation product:

$$Cr^{3+}(aq) + 3OH^{-}(aq) \rightarrow Cr(OH)_3(ppt) \qquad (3)$$

As expected, the thicker polymer, which contained more reduced units, reduced more Cr(VI) and at a faster rate. Following 60 min of exposure, the thick polymer had reduced 84% of the Cr(VI) present while the thin polymer had only reduced 28% of the Cr(VI). As these thick polymers contain small amounts of degradation products (Figure 1b), the possibility of these degradation products influencing the reduction of Cr(VI) was investigated by following the reduction of Cr(VI) at a degraded thin polyaniline film. Identical data were recorded for the pure and degraded thin polyaniline films, indicating that slight degradation of the polymer has no influence on the reduction of Cr(VI).

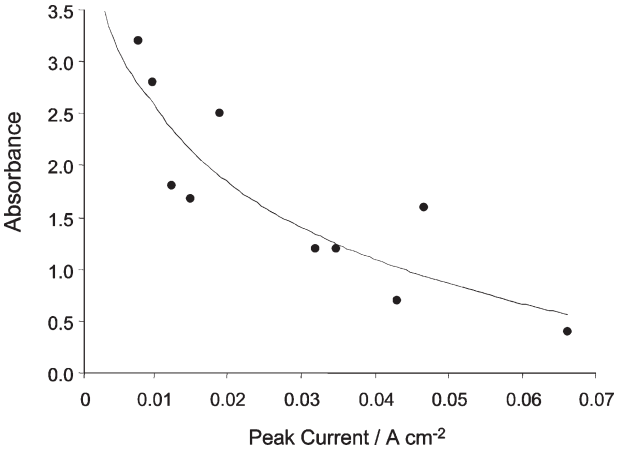


FIGURE 3. Plot of absorbance at 246 nm after 180 min immersion period against polymer peak current of the leucoemeraldine/emeraldine transition.

At immersion times of 80−90 min, an additional band emerges at 246 nm and while the intensity of the bands at 351 and 260 nm decreases as a function of the exposure period, this absorbance at 246 nm increases (Figure 2). The formation of this band at 246 nm obscures any further reduction of the 260 nm band. This band is not associated with the hexaaquochromium(III) complex, which has weak absorption bands centered at 410 and 580 nm.

It is clear from the absorbance values shown in Figure 2a that the transition at 246 nm has a high extinction coefficient. Interestingly, this absorbance at 246 nm increases at a much faster rate during immersion experiments of thin polymers where incomplete Cr(VI) reduction is achieved (28% over a 1-h period). A plot of the absorbance at 246 nm after 180 min of immersion against the peak current of the leucoemeraldine/emeraldine transition shown in Figure 3 emphasizes the correlation between the two. It is seen that the absorbance is much lower for the polymers grown to greater thickness, indicating that the species absorbing at this wavelength are formed at a much slower rate for these thick polyaniline films.

Given the fact that this peak is only observed under conditions where the Cr(VI) reduction reaction is less efficient, then it could be connected to the presence of Cr(V) or Cr(IV) species. These higher oxidation states may occur when the thin polymer is driven into a higher oxidation state (typically 80 min) and is no longer able to provide the high driving force to convert the Cr(VI) to Cr(III) (eq 1). Although it is well-accepted that there are no stable compounds of Cr(V) or Cr(IV) (*21*), there is kinetic evidence that one-electron reduction of $HCrO_4^-$ in acid solution gives H_3CrO_4 (*22*). More stable Cr(IV) intermediates were observed on reduction of CrO_3 by citric acid (*23*). More recently, Mytych et al. (*24*) have identified transient Cr(V) and Cr(IV) species during the photochemical reduction of Cr(VI) by aliphatic alcohols using flash photolysis techniques. Moreover, the Cr(V) species were found to have high absorptions at wavelengths in the region of 250 nm, which compare well with the λ_{max} of 246 nm in Figure 2. Consequently, this absorption at 246 nm appears to be connected with the formation of Cr(V) species.

Nevertheless, these Cr(V) species are short-lived, but they may be stabilized under these experimental conditions through the formation of a Cr(V)−polyaniline charge-transfer complex. The only other chromium-containing species that are known to absorb in the near UV region are peroxo

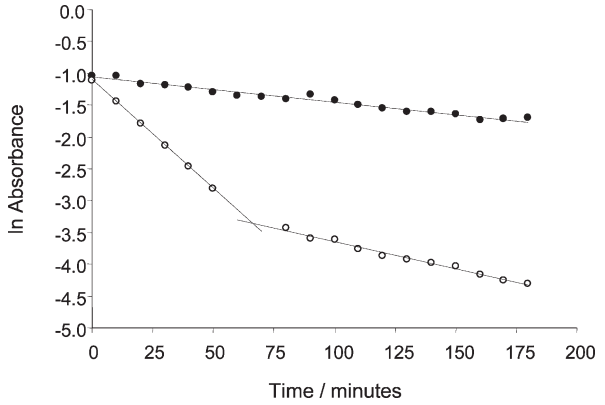


FIGURE 4. Pseudo-first-order kinetics plot of the logarithm of the absorbance as a function of time for Cr(VI) reduction at a (●) "thin" (peak current 9 × 10^{-3} A) and a (○) "thick" (peak current 76 × 10^{-3} A) polymer film.

compounds of Cr(III), which are formed when molecular oxygen is in excess (*25*):

$$Cr^{2+} + O_2 \rightarrow CrO_2^{2+} \quad (4)$$

Obviously, this peroxo compound cannot be formed in these experiments. Indeed, the absorbance peak at 246 nm was observed regardless of whether the solution was deoxygenated or oxygenated.

Kinetics as a Function of Film Thickness and Oxidation State. From eq 1, it is seen that the rate of the reaction can depend on three different species: $HCrO_4^-$, H^+, and $Pani^0$. Accordingly, the rate law for the reduction reaction may be expressed by eq 5, where k is the rate constant and the exponents (m, n, and p) are the reaction orders with respect to each reactant:

$$R = k[HCrO_4^-]^m[Pani^0]^n[H^+]^p \quad (5)$$

Since the concentration of Cr(VI) is low and will be the limiting reactant, then the rate law can be reduced to eq 6, where k' represents a pseudo-first-order rate constant:

$$R = k'[HCrO_4^-]^1 \quad (6)$$

In Figure 4, representative kinetic plots are shown for two polyaniline films; one representing a thin coating of polyaniline and the other a thick coating of polyaniline. It can be seen from these plots that reduction at the thin polyaniline film obeys pseudo-first-order kinetics for the duration of the 200-min measurement period. Typical values for the pseudo-first-order rate constant for the thin polymer were 0.0039 min^{-1}. This first-order behavior is in agreement with reports in the literature in which Cr(VI) has been reduced at a polypyrrole-coated carbon substrate (*9*, *12*), reduced by hydrogen peroxide (*26*), reduced by iron (*27*), and reduced by hydrogen sulfide (*28*). However, this is not the case for the thick polyaniline films. Reduction at these surfaces proceeds by a two-stage process. Each individual stage obeys pseudo-first-order kinetics, but there is considerable variation in the pseudo-first-order rate constants with a much higher rate of reaction being observed in the early stages of immersion. Second, the rate constants for each of the two-stage processes were a function of the polymer thickness, highlighting the importance of surface area in the redox reaction. This is shown clearly in Figure 5a,b, where the pseudo-first-order rate constants for the first stage, k'_{Pani1}, and the second phase, k'_{Pani2}, are plotted as a function of the thickness of the polymer, respectively. Again, the thickness of the polymer is expressed in terms of the peak currents recorded for the

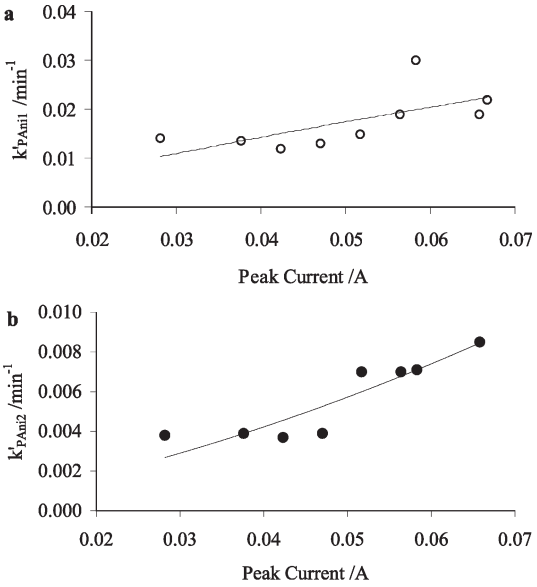


FIGURE 5. (a) Pseudo-first-order rate constant, k'_{Pani1}, plotted as a function of the polymer thickness expressed in terms of the peak current measured for the leucoemeraldine to emeraldine transition. (b) Pseudo-first-order rate constant, k'_{Pani2}, plotted as a function of the polymer thickness expressed in terms of the peak current measured for the leucoemeraldine to emeraldine transition.

leucoemeraldine to the emeraldine redox transition in the aniline-free solution. It can be seen from these plots that there is a general increase in the pseudo-first-order rate constants with increasing film thickness. Although a two-stage process was observed generally for the polymers with peak currents higher than 19 × 10^{-3} A cm^{-2}, there were some instances where a one-stage process was observed with peak currents in the region of 37 × 10^{-3} A cm^{-2}, showing that the transition in the kinetics occurs for polymers grown to give peak current densities between 19 × 10^{-3} and 37 × 10^{-3} A cm^{-2}.

A possible explanation for this two-stage behavior may be given by the redox chemistry of polyaniline. The reduction of Cr(VI) by polyaniline has previously been described by eq 1. In the reaction, polyaniline is transformed from the fully reduced form, leucoemeraldine to the partially oxidized emeraldine form. However, it is possible that the polyaniline becomes oxidized further from the emeraldine to the pernigraniline state inducing further Cr(VI) reduction. This reaction is given in eq 7, where $Pani^{4+}$ and $Pani^{2+}$ represent the pernigraniline and emeraldine oxidation states of polyaniline, respectively:

$$2HCrO_4^-(aq) + 14H^+ + 3Pani^{2+}(s) \rightarrow 2Cr^{3+}(aq) + 3Pani^{4+}(s) + 8H_2O(l) \quad (7)$$

Therefore, the variation in the kinetics of the Cr(VI) reduction at the thin and thick polymer films could be associated with the fact that reduction at the thin polymer involves a change in the redox state of the polymer from the leucoemeraldine to the pernigraniline state (eqs 1 and 7), but reduction at the thick polymer film involves a clear two-stage process. The thick polymer is first oxidized from the leucoemeraldine to the emeraldine state and then after some time period, further oxidation of the polymer to the higher pernigraniline oxidation state (eq 7) occurs. In this latter case, k'_{Pani1}, represents the pseudo-first-order rate constant for the Cr(VI) reduction and the concomitant oxidation of the polymer from the leucoemeraldine to the emeraldine states. Likewise, k'_{Pani2}, represents the pseudo-first-order rate constant for the Cr(VI) reduction reaction and oxidation

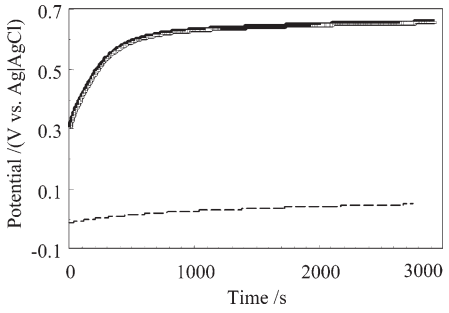


FIGURE 6. Open-circuit potential recorded during the reduction of Cr(VI) in a 0.125 mmol dm^{-3} $Na_2Cr_2O_7$ in 0.1 mol dm^{-3} H_2SO_4 solution at a "thin" polyaniline film (peak current density of 9 × 10^{-3} A) (– –) and a "thick" polyaniline film (peak current density of 76 × 10^{-3} A) (—).

of the polymer from the emeraldine to the higher pernigraniline redox states. The pseudo-first-order rate constant, k'_{Pani2}, is lower than k'_{Pani1} indicating that the higher oxidation state of polyaniline is less effective in reducing the Cr(VI).

Direct evidence to support the view that the two-phase process, as seen in Figure 4, is connected with the different oxidation states of polyaniline was obtained by recording the open-circuit potential of the polyaniline during the Cr(VI) reduction reaction. Typical data are shown in Figure 6 for two polymer systems grown to give final peak currents of 76 × 10^{-3} and 9 × 10^{-3} A. In the case of the thick polymer (76 × 10^{-3} A), the open-circuit potential varied from about 0.0 to 0.05 V(Ag/AgCl) during the 50-min period. This potential variation is consistent with a large proportion of the polymer being maintained in the reduced state, and accordingly, the Cr(VI) reduction reaction involves the transformation of the polymer from the leucoemeraldine to the emeraldine state (eq 1). In contrast, the thin polymer (9 × 10^{-3} A) is oxidized rapidly on contact with the Cr(VI) solution. The initial potential was recorded as 0.3 V(Ag/AgCl), being consistent with the emeraldine state of the polymer (Figure 1). On further oxidation in the Cr(VI) solution, the potential reaches values approaching 0.7 V(Ag/AgCl), which are now consistent with the polymer being converted to the higher pernigraniline state (eq 7). Interestingly, on further immersion, the open-circuit potential of the thick polymer reaches values in the region of 0.7 V(Ag/AgCl), indicating the participation of the second redox state of the polymer in the Cr(VI) reduction reaction.

Further evidence to support this two-stage oxidation of the polymer was obtained by studying the activity of a partially oxidized thick polymer in the reduction of Cr(VI). Oxidation of the polymer was achieved by polarization at 0.4 V (Ag/AgCl) for 60 min. This procedure ensured that the polymer was converted fully to the emeraldine state. This partially oxidized polymer was then immersed in the acidified Cr(VI) solution, and the kinetics of the reduction reaction was monitored. A pseudo-first-order rate plot was obtained with a rate constant of 2.4 × 10^{-3} min^{-1}. This low rate constant is typical of the k'_{Pani2} values shown in Figure 5b. Second, the absence of a two-stage process for this partially oxidized thick polymer is further evidence of the participation of both redox states of polyaniline in the Cr(VI) reduction reaction.

This difference in the manner in which the thin and thick polymer films catalyze the Cr(VI) reduction reaction is probably related to energy considerations and to the nature and morphology of the films formed under these different experimental conditions. In terms of energy considerations, the experimental data of MacDiarmid and co-workers (*29*) of the standard reduction potentials of the leucoemeraldine/emeraldine (LE/ES) and the emeraldine/pernigraniline (ES/PN) couples as a function of pH (eqs 8 and 9) were used to

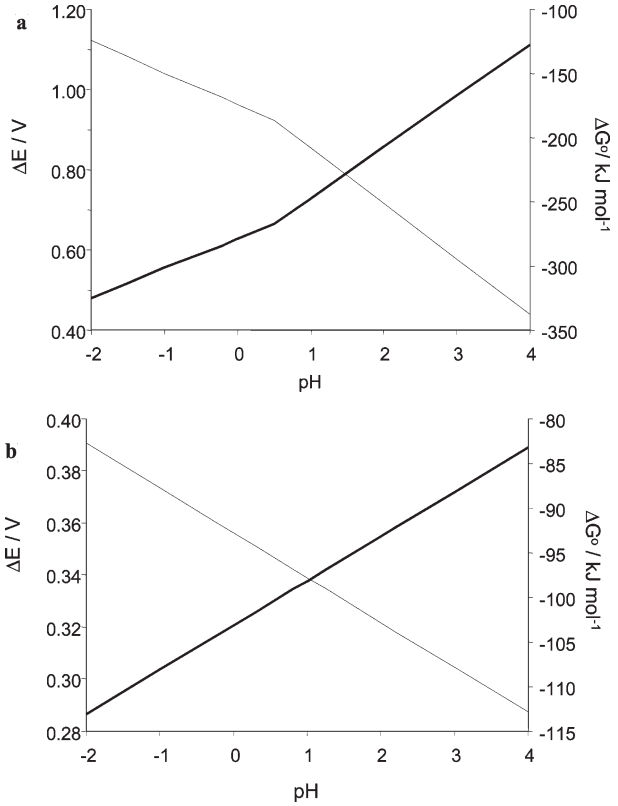


FIGURE 7. Variation of ΔE (– –) and ΔG° (—) as a function of pH for the Cr(VI)–polyaniline electrolytic cell (a) for the leucoemeraldine/emeraldine redox couple and (b) the emeraldine/pernigraniline redox couple.

generate a plot of the redox potential and free energy of the polyaniline–Cr(VI) redox reaction:

$$\text{LE/ES:} \quad E = 0.1298 - 0.058\ \text{pH} \tag{8}$$

$$\text{ES/PN:} \quad E = 0.736 - 0.120\ \text{pH} \tag{9}$$

In the work of MacDiarmid and co-workers, the first polyaniline redox couple (LE/ES) was found to vary according to eq 8 up to a pH of 0.5 only. Above this pH, the reduction potential was found be invariant at 0.1 V/(RHE). The reduction potential of the second redox couple (ES/PN) behaved linearly with pH over the entire range examined, according to eq 9.

The plot of redox potential and free energy as a function of pH is presented in Figure 7, where the traces shown in Figure 7a were obtained using the LE/ES transition of the polymer, while the traces shown in Figure 7b were generated using the ES/PN redox states of the polymer. In both cases, the driving force for the reaction is greater under acidic conditions in agreement with previous reports (*30*). However, it is also seen that more negative free energy changes occur for participation of the leucoemeraldine/emeraldine couple rather than the emeraldine/pernigraniline couple, indicating that the thermodynamics of the reaction depend on the oxidation state of polyaniline.

In terms of the polymer morphology, it is well-known that thin polymer films are compact, but with continued growth a more porous layer is formed (*31*). This porous structure will provide a much higher surface area for the Cr(VI) reduction reaction, which is consistent with the higher rates of Cr(VI) reduction observed for the thick polymers as compared to the thin polymers (Figures 2 and 4). Also, the variation of the rate constants with the thickness of the polymers (Figure 5a,b) shows clearly that the kinetics of the

reaction depends on the surface area of the polymer, being consistent with a heterogeneous surface reaction. Under these conditions, the Cr(VI) species are in direct contact with much of the polyaniline surface. Initially, the high surface area of the polymer exposed to the Cr(VI) solution is such that the polymer is driven only to the emeraldine oxidations state (eq 1 and Figure 6). As the polymer is converted to the emeraldine state, then further reduction of the Cr(VI) occurs through oxidation of the polymer from the emeraldine to pernigraniline state (eq 7). This redox transition is less efficient in reducing the Cr(VI) giving a lower rate of reduction (Figures 4 and 5).

Conversely, the more compact thin layers restrict the access of the Cr(VI) to the outer surface of the polymer, and under these conditions only the outer surface of the polymer is oxidized initially giving a much lower rate of Cr(VI) reduction. In addition, the highly oxidizing Cr(VI) solution rapidly converts the outer layers of the polymer to the emeraldine oxidation state, as evident from the open-circuit potential profile (Figure 6). Consequently, the two-phase process is not observed; only the oxidation of the polymer from the emeraldine to the pernigraniline state is observed. Eventually, the bulk polymer will become oxidized, as the outer oxidized layer will induce oxidation of the inner polyaniline layers. The appearance of the absorption band at 246 nm following 80 min of immersion (Figure 2), which was attributed to the presence of Cr(V) is consistent with this analysis. As the thin and compact polyaniline layer is driven to the higher pernigraniline oxidation state, it becomes less efficient in converting the Cr(VI) to Cr(III). Accordingly, only partial reduction of Cr(VI) is observed.

Acknowledgments

S.T.F. acknowledges the support of a Daniel O'Connell Scholarship from the National University of Ireland Maynooth and a scholarship from Enterprise Ireland.

Literature Cited

(1) Katz, S. A.; Salem, H. *The Biological and Environmental Chemistry of Chromium*; VCH Publishers: New York, 1994; pp 51−58.
(2) Srivastava, S.; Prakash, S.; Srivastava, M. M. *Biometals* **1999**, *12*, 201.
(3) Seaman, J. C.; Bertsch, P. M.; Schwallie, L. *Environ. Sci. Technol.* **1999**, *33*, 938.
(4) Higgins, T. E.; Halloran, A. R.; Petura, J. C. *J. Soil Contam.* **1997**, *6*, 767.
(5) Melitas, N.; Chuffe-Moscoso, O.; Farrell, J. *Environ. Sci. Technol.* **2001**, *35*, 3948.
(6) Martinez, S. A.; Rodriguez, M. G.; Barrera, C. *Water Sci. Technol.* **2000**, *42*, 55.
(7) Wei, C.; German, S.; Basak, S.; Rajeshwar, K. *J. Electrochem. Soc.* **1993**, *140*, L60.
(8) Wampler, W. A.; Rajeshwar, K.; Pethe, R. G.; Hyer, R. C.; Sharma, S. C. *J. Mater. Res.* **1995**, *10*, 1811.
(9) Senthurchelvan, R.; Wang, Y.; Basak, S.; Rajeshwar, K. *J. Electrochem. Soc.* **1996**, *143*, 44.
(10) Alatorre, M. A.; Gutierrez, S.; Paramo, U.; Ibanez, J. G. *J. Appl. Electrochem.* **1998**, *28*, 551.
(11) Desimoni, E.; Bassani, I. *Anal. Commun.* **1999**, *36*, 45.
(12) Rodriguez, F. J.; Gutierrez, S.; Ibanez, J. G.; Bravo, J. L.; Batina, N. *Environ. Sci. Technol.* **2000**, *34*, 2018.
(13) Malinauskas, A.; Holze, R. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 982.
(14) Yang, Y. J.; Huang, H. J. *Anal. Chem.* **2001**, *73*, 1377.
(15) Mirmohseni, A.; Oladegaragoze, A. *J. Appl. Polym. Sci.* **2002**, *85*, 2772.
(16) Desimoni, E.; Brunetti, B.; Ugo, P.; Cazzaniga, R. *Synth. Met.* **2002**, *130*, 135.
(17) Chen, W. C.; Wen, T. C.; Gopalan, A. *Electrochim. Acta* **2002**, *47*, 4195.
(18) Hu, C. C.; Chen, E.; Lin, J. Y. *Electrochim. Acta* **2002**, *47*, 2741.
(19) Dinh, H. N.; Ding, J. F.; Xia, S. J.; Birss, V. I. *J. Electroanal. Chem.* **1998**, *459*, 45.
(20) Dinh, H. N.; Birss, V. I. *J. Electroanal. Chem.* **1998**, *443*, 63.
(21) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley: New York, 1980.
(22) Espenson, J. H. *Acc. Chem. Res.* **1970**, *3*, 347.
(23) Krumpolc, M.; Rocek, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.
(24) Mytych, P.; Karocki, A.; Stasicka, Z. *J. Photochem. Photobiol. A: Chem.* **2003**, *160*, 163.
(25) Palopoli, C.; Signorella, S.; Sala, L. F. *New J. Chem.* **1997**, *21*, 343.
(26) Pettine, M.; Campanella, L.; Millero, F. J. *Environ. Sci. Technol.* **2002**, *36*, 901.
(27) Alowitz, M. J.; Scherer, M. M. *Environ. Sci. Technol.* **2002**, *36*, 299.
(28) Kim, C.; Zhou, Q. H.; Deng, B. L.; Thornton, E. C.; Xu, H. F. *Environ. Sci. Technol.* **2001**, *35*, 2219.
(29) Huang, W. S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans.* **1986**, *82*, 2385.
(30) Ku, Y.; Jung, I. L. *Water Res.* **2001**, *35*, 135.
(31) Rossberg, K.; Paasch, G.; Dunsch, L.; Ludwig, S. *J. Electroanal. Chem.* **1998**, *443*, 49.

Received for review January 28, 2004. Revised manuscript received June 16, 2004. Accepted June 18, 2004.

ES0498585