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Reduction of hexavalent chromium at a polypyrrole-coated aluminium electrode: Synergistic interactions

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Abstract

Adherent polypyrrole films were electropolymerized from a tosylic acid solution onto an aluminium substrate and used for the reduction of Cr(VI). The reduction of Cr(VI) to the trivalent state was found to proceed by pseudo-first-order kinetics with an activation energy barrier of 15.13 kJ mol^{-1}. This catalyst could be regenerated by reducing the composite at a sufficiently negative potential, in the absence of Cr(VI). However, it was found that the catalyst functioned also through a self-sustained regeneration mechanism. In this mechanism, Cr(VI) was reduced by PPy^0 to generate PPy^+, but the PPy^+ was subsequently reduced to PPy^0 by oxidation of the aluminium substrate, thus regeneration of the catalytic PPy^0 surface giving rise to a synergistic action between the polypyrrole and the aluminium substrate.

1. Introduction

Chromium is found in group-six of the periodic table and has the ability to form stable complexes in a range of oxidation states from −2 to 6. Of these Cr(III) and Cr(VI) are the most common, with the hexavalent form being toxic, carcinogenic and extremely mobile [1]. Nevertheless, hexavalent chromium is generated in a number of processes, such as leather tanning, corrosion inhibition and chrome plating. Consequently, there is an ever-increasing interest in developing procedures for the removal of toxic hexavalent chromium from the environment. 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 at a variety of inorganic and organic materials at neutral pH [2]. Furthermore, the trivalent chromium can be isolated as insoluble Cr(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 treatments direct reduction, to the trivalent state, is achieved through the application of suitable electrode potentials.

More recently, it has been shown that conducting polypyrrole films can be used to reduce Cr(VI), opening up the possibility of a new remediation-control technology [7–12]. Polypyrrole (PPy) is a well-known conducting polymer and can undergo good reversibility between its conducting and insulating states. During reduction, anionic sites are formed that require cations for charge compensation (or anion expulsion) while upon oxidation, cationic sites such as polarons (PPy^+) and bipolarons (PPy^{2+}), are formed on the polypyrrole chains.

The first report of the reduction of hexavalent chromium at a conducting polymer matrix was made in 1993 by Rajeshwar and co-workers [7–9] who observed the reduction of hexavalent chromium at a polypyrrole electrode, with approximately 100% efficiency, and at time intervals spanning only minutes. Furthermore, the reversibility of the polymer redox process enabled the electrochemical recycling of the polypyrrole for repeated treatment of Cr(VI). Since that time other studies have been reported on the use of polypyrrole in the reduction of Cr(VI) [10–12]. In each of these studies, inert substrates have been chosen in the preparation of the polypyrrole electrodes and there have been no reports on the participation of the substrate in the Cr(VI) reduction reaction.

In this paper a substrate with a high driving force for oxidation is chosen. Pyrrole was electropolymerized at a pure aluminium substrate to generate a polypyrrole-coated aluminium electrode. This composite was then employed in the reduction of hexavalent chromium to the less toxic trivalent state. The electrosynthesized polypyrrole coating was first reduced and then exposed to the hexavalent solution and the reduction of the hexavalent chromium monitored as a function of the exposure period.

2. Experimental

Prior to electropolymerization, the samples, 99.9999% aluminium, were polished to a smooth surface finish, using successively finer grades of SiC paper, rinsed and dried in an air stream. In all tests, aluminium samples, with a surface area of 0.785 cm^2, were used.

The PPy films were grown potentiostatically at 1.25 V(SCE) on the aluminium electrodes from aqueous solutions containing 0.2 mol dm^{-3} pyrrole and 0.1 mol dm^{-3} tosylic acid in a three-electrode cell. An EG&G potentiostat Model 263 or a Solartron EI 1287 electrochemical interface was used as the potentiostat. A saturated calomel electrode was used as reference and high-density graphite rods were employed as the counter electrode. After growth, the films were rinsed with distilled water and then reduced in 0.1 mol dm^{-3} sulphuric acid at −0.945 V(SCE) for a period of 30 min. This was to ensure that the polymer was in its reduced state. The films were then washed and transferred to an acidified Cr(VI) solution (15.0 cm^3, with a concentration range of 3.5×10^{-5} to 6.7×10^{-3} mol dm^{-3} in Cr(VI) in 0.1 mol dm^{-3} H_2SO_4) and the concentration of Cr(VI) was monitored under open circuit potential conditions.

Reduction of the hexavalent chromium was monitored using a spectrophotometric technique. Samples were withdrawn at regular time intervals and the UV-Vis absorption spectra, between 200 and 800 nm, were measured using a Cary 50 UV-Vis spectrometer. The concentration of Cr(VI) was calculated from the intense Cr(VI) charge transfer band at 350 nm.

The electrochemical behaviour of the polypyrrole-coated aluminium samples was studied prior to and following the Cr(VI) reduction process using cyclic voltammetry. Voltammograms were recorded between −200 and 800 mV(SCE) at 50 mV s^{-1}.

3. Results and discussion

A typical plot depicting the growth of polypyrrole on pure aluminium is shown in Figure 1. For comparative purposes, the oxidation of pure aluminium in a pyrrole-free tosylic acid solution is also shown. In the absence of pyrrole, the current-time transient is characterized by a rapid decrease in the current during the first 50 s and then a more gradual decrease in current as the electrode is passivated in the acid solution. In contrast, the current-time behaviour is very different in the presence of pyrrole. The current initially decreases sharply, but then increases to reach a peak value of 6.0 mA before decaying to a near steady-state value. This behaviour is consistent with the initial oxidation of the pyrrole monomer and the nucleation and growth of the polymer film in agreement with previous studies where polypyrrole has been formed electrochemically at an aluminium substrate [13, 14]. This procedure gave rise to adherent and smooth polypyrrole deposits that could only be removed on mechanical polishing. The thickness of the polypyrrole coating was estimated as 17–18 μm, using the relationship that 600 mC cm^{-2} corresponds to a 1.0 μm thick polypyrrole film [15].

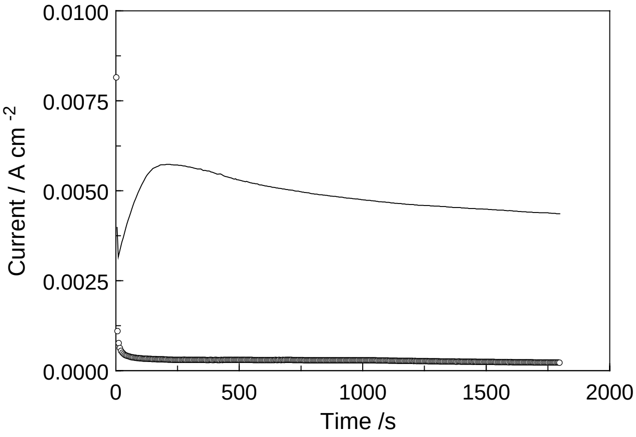

Fig. 1. Current-time transients recorded for Al polarized at 1.25 V(SCE) ○ in a 0.1 mol dm^{-3} tosylic acid solution and – in 0.1 mol dm^{-3} tosylic acid and 0.3 mol dm^{-3} pyrrole.

Following formation of the polymer at the aluminium electrode, the polymer was reduced in the sulphuric acid solution in accordance with Equation 1.

$$PPy^{+}_{(s)} + e^{-} \rightarrow PPy^{0}_{(s)} \tag{1}$$

Here, the 0 and + superscripts correspond to the reduced and oxidized states of the polypyrrole respectively. This reduced polymer-coated electrode was then immersed in acidified solutions of varying dichromate concentration. These acidic conditions were employed as it is well known that the reduction of Cr(VI) proceeds more efficiently under acidic conditions, and indeed this has been observed with polypyrrole-coated carbon electrodes [9]. Typical UV-visible spectra showing the uptake and reduction of Cr(VI) during contact with the polymer-modified electrode are shown in Figure 2. The charge transfer band centred at 350 nm for the $Cr_2O_7^{2-}$

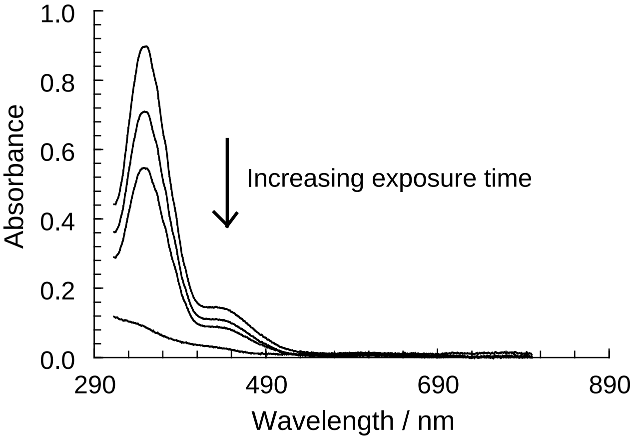

Fig. 2. UV-visible spectra recorded for an acidified Cr(VI) solution as a function of the exposure time to the polypyrrole-coated electrode. Data were recorded at time intervals of 0, 275, 350 and 600 min.

complex can be seen clearly. It is also clear that the absorbance decreases with increasing exposure time. These data were recorded in a 1.34×10^{-3} mol dm^{-3} Cr(VI) solution at 0, 275, 350 and 600 min and it can be seen that the absorbance decreases considerably between these time intervals. At lower Cr(VI) concentrations (for example 1.66×10^{-4} mol dm^{-3}) complete disappearance of the dichromate band was observed following 100 min; this was accompanied by a gradual change in the colour of the dichromate solution from orange-like to almost colourless. This removal of Cr(VI) is consistent with the reduction of the hexavalent chromium to the stable trivalent state with the resultant oxidation of the polymer in accordance with Equation 2.

$$\begin{aligned} &Cr_2O_{7(aq)}^{2-} + 14H^+ + 6PPy_{(s)}^0 \\ &\quad \rightarrow 2Cr_{(aq)}^{3+} + 6PPy_{(s)}^+ + 7H_2O_{(l)} \end{aligned} \quad (2)$$

Indeed, it was possible to detect the Cr(III) complex, by recording the UV-visible spectrum of a 6.7×10^{-3} mol dm^{-3} Cr(VI) solution exposed to a polypyrrole-coated electrode for a period exceeding 800 min. This shows that the reduced Cr(III) is released into the solution environment, and although some may be trapped within the polymer, large amounts of Cr(III) are released into the solution phase.

This reduction process was found to obey pseudo-first-order kinetics. This 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 [16], reduced by iron [17] and reduced by hydrogen sulphide [18]. The rate law, for the dichromate reduction reaction, may be expressed as Equation 3.

$$R = k[\mathrm{Cr(VI)}]^1[\mathrm{PPy}^0]^m[\mathrm{H}^+]^p \quad (3)$$

However, since the acid is in excess (0.1 mol dm^{-3}) and assuming that the concentration of PPy^0 remains high and is invariant relative to the levels of Cr(VI), then Equation 3 may be reduced to Equation 4 where k^1 represents a pseudo-first-order rate constant.

$$R = k^1[\mathrm{Cr(VI)}]^1 \quad (4)$$

A typical pseudo-first-order plot showing the logarithm of the Cr(VI) concentration as a function of time is shown in Figure 3. This reasonable adherence to pseudo-first-order kinetics indicates that the concentration of PPy^0 remains essentially constant throughout the duration of the experiments. The pseudo-first-order rate constant (k^1) was found to be 2.3×10^{-3} min^{-1}. Although this low value is indicative of a slow reaction, it is partly connected, also, with the low surface area of the polymer exposed to the solution (0.785 cm^2), as the reduction of Cr(VI) is a surface phenomenon. Indeed, Wampler et al. [19] have shown that the Cr(VI) conversion is best expressed per unit geometric surface of the sample.

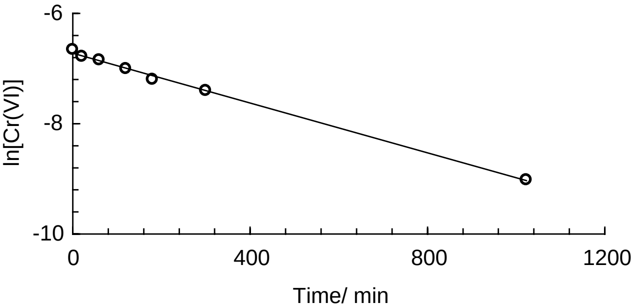

Fig. 3. First-order kinetics plot showing the logarithm of the concentration of Cr(VI) plotted as a function of time.

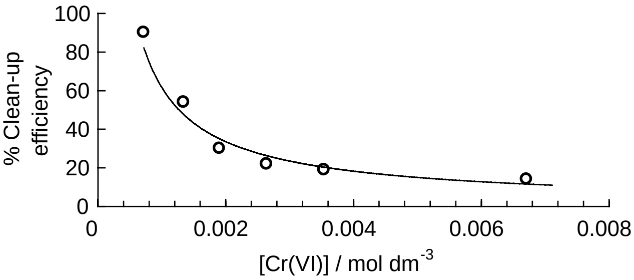

Fig. 4. Clean-up efficiency, expressed as a % of the initial concentration and calculated following a 180 min exposure period, plotted as a function of the initial concentration of Cr(VI).

Using various initial concentrations of Cr(VI), the rate of reduction was monitored as a function of temperature. Using the Arrhenius equation, the activation energy was computed as 15.13 kJ mol^{-1}. Again, this represents a relatively high value for the activation energy.

Data showing the clean-up efficiency of the polypyrrole-modified Al electrode, measured over a 180-min exposure period, are shown in Figure 4. Near to 100% reduction efficiencies occur with the more dilute Cr(VI) solutions, but the efficiencies are much lower, for these short periods, with the more concentrated solutions. However, even with these more concentrated solutions, for example, 6.7×10^{-3} mol dm^{-3} Cr(VI), complete reduction i.e. 100% reduction efficiency was observed after 830 min of exposure. These findings are consistent with a slow but continued uptake and reduction of Cr(VI), and are indicative of a regeneration process or mechanism. Clear evidence in support of this was obtained by calculating the theoretical number of PPy^0 sites and assuming a 100% reduction efficiency, the maximum amount of Cr(VI) that should be reduced. For example in a typical reaction, for instance the 1.342×10^{-3} mol dm^{-3} Cr(VI) solution (15 cm^3), the number of PPy$^+$ sites was calculated as 4.15×10^{-5} mol of PPy units using Faraday's law and the electrosynthesis charge. Assuming a doping level of 0.3 (i.e. one positive charge per three rings [19]) then the number of trimers can be computed as 1.38×10^{-5} mol. Since a trimer is involved in the redox reaction $PPy^0 \rightarrow PPy^+ + e^-$, then the number of PPy$^+$sites is also equal

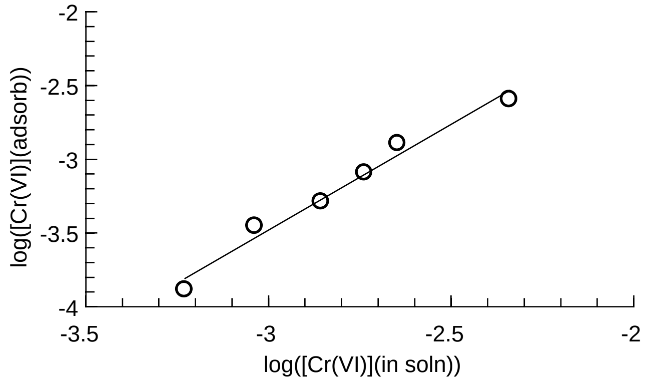

Fig. 5. Freundlich isotherm plot showing the logarithmic dependence between the concentrations of the adsorbed Cr(VI) and Cr(VI) in solution.

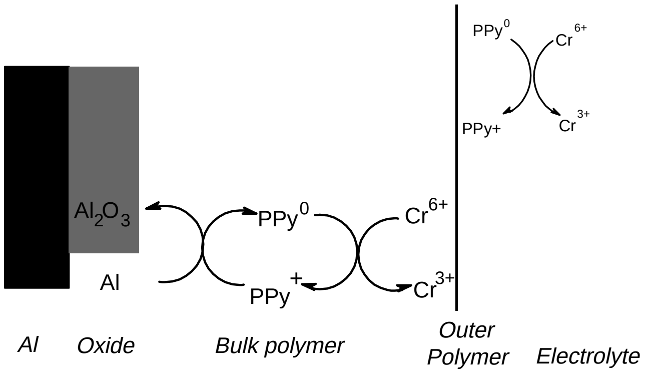

Fig. 6. Schematic plot depicting the reactions, which occur in the regeneration mechanism.

to 1.38×10^{-5} mol. Assuming 100% reduction efficiency and using a stoichiometric ratio of $3PPy^0$ to $1Cr^{6+}$, then the theoretical amount of Cr^{6+}removed should be 23%. However, the actual amount of Cr^{6+} removed was 94% following a 300 min immersion period. Indeed, this will approach 100% if exposed for an additional time period. This large discrepancy between the theoretical and actual amounts lies well outside any possible error in the estimation of the film thickness and the number of PPy^+ sites. Consequently, the reduction of Cr(VI) must also proceed by another additional route or through a regeneration mechanism.

Further evidence in support of such a regeneration mechanism was obtained by fitting the Cr(VI) reduction data for the polypyrrole-coated electrode to the Freundlich isotherm. This is shown by the linear dependence between the logarithm of the concentration of the adsorbed Cr(VI) and the logarithm of the concentration of the free Cr(VI) in solution, as presented in Figure 5. This isotherm, for adsorption from solution, can be represented by the relationship,

$$\frac{x}{m} = kc^{1/n} \tag{5}$$

where k and n are empirical constants, with the value of n usually less than unity, x represents the amount of solute adsorbed by mass m of solid, while c represents the concentration of the solute species in solution. Assuming that Cr(VI) is first adsorbed prior to reduction, then x can be equated with the concentration of reduced Cr(VI), while c corresponds to the original concentration of Cr(VI) in solution. In these experiments the initial concentration of Cr(VI) was varied. The concentration of Cr(VI) remaining in solution following a 120 min immersion period was then determined and equated with x. This isotherm is based on the principle that saturation of the surface does not occur, i.e. the amount adsorbed increases with increasing concentration, suggesting that the PPy^0 sites are in excess during these reduction experiments. Given the relatively small surface area used in these experiments coupled with the relatively high Cr(VI) concentrations, then saturation of the PPy^0 surface should be achieved easily unless the surface is regenerated enabling further adsorption and reduction.

This regeneration, or synergistic, mechanism can be represented by the diagram depicted in Figure 6. At the polymer-solution interface direct electron transfer between the PPy^0 and Cr(VI) occurs resulting in reduction of the hexavalent chromium to the trivalent state. However, the oxidized polypyrrole in contact with the aluminium substrate generates a galvanic couple enabling the regeneration of the reduced polypyrrole in accordance with Equation 6.

$$Al + 3PPy^+ \rightarrow Al^{3+} + 3PPy^0 \tag{6}$$

This represents a thermodynamically feasible reaction with a free energy of −490.63 kJ mol^{-1} (computed from the standard reduction potentials of the $Al|Al^{3+}$ and $PPy^0|PPy^+$couples). This aluminium oxidation half reaction gives rise to the production of aluminium oxide or hydrated aluminium oxide as shown in the diagram. Indeed, evidence for the participation of this reaction for the polypyrrole-coated electrode could be seen on removing the polypyrrole coating from the aluminium substrate following extended immersion in the Cr(VI) solution. A thick white layer could be observed on the aluminium, which is consistent with an aluminium oxide layer, Al_2O_3, with aluminium in the trivalent state. The reduction couple gives rise to the regeneration of the reduced polypyrrole, which can now participate in the reduction of the hexavalent chromium, providing a self-sustained regeneration of the catalyst. It is interesting to note that although this regeneration of the catalyst results in an increase in the thickness of the aluminium oxide layer, detachment of the polymer from the substrate does not occur, at least not for time intervals up to 35 days.

As shown in Figure 6, the Cr(VI) species may be reduced also within the outer layers of the polymer film. However, it is unlikely that the Cr(VI) species will travel to any great extent within the bulk polymer. Indeed, Senthurchelvan et al. [9] have concluded from their

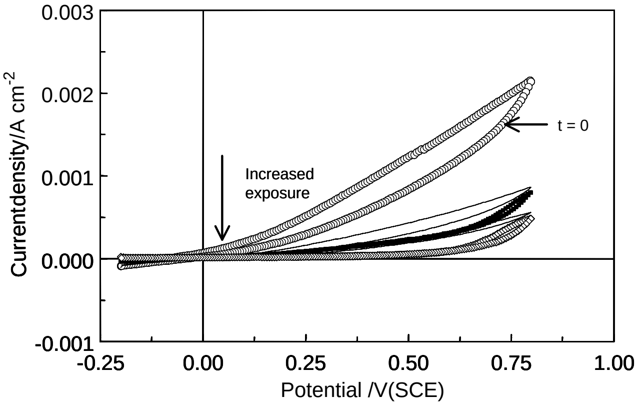

Fig. 7. Cyclic voltammograms recorded for the polypyrrole-coated aluminium electrode following exposure to 125 cm^3 of a 1.3 x 10^{-3} mol dm^{-3} Cr(VI) solution. Data recorded following 0, 1, 2, 33, 58 and 830 h.

studies, on the efficiency of a polypyrrole-coated carbon catalyst, that only the external surface of the polymer is easily accessible to the Cr(VI) species. Further conversion of the Cr(VI) is limited by the penetration of Cr(VI) and the reaction zone into the bulk of the polymer.

The electrochemical activity of the polypyrrole-coated electrode as a function of the exposure period to the Cr(VI) solution is shown in Figure 7. In this figure, cyclic voltammograms are presented, recorded at 50 mV s^{-1}, between the potential limits of −200 and 800 mV(SCE). These data were recorded following 0, 1, 2, 33, 58 and 830 h of exposure to a 1.3×10^{-3} mol dm^{-3} Cr(VI) solution. On comparison of these voltammograms, a clear reduction in the measured current can be seen between the voltammogram recorded at time = 0 and the subsequent periods. This reduction in the anodic current may be connected with the degradation of the polymer or with the formation of aluminium oxide, giving rise to a semi-insulating interface between aluminium and the polypyrrole coating. The presence of a semi-insulating layer may impede charge transport to the outer layers. Long term immersion experiments, which involved exposing Al-PPy to a concentrated solution of Cr(VI) for over a month showed no visible signs of degradation, suggesting that the decrease in current is probably more connected with the oxidation of the aluminium substrate than degradation of the polymer.

In addition, it was possible to regenerate these composites by reducing the polypyrrole. Again, this suggests that the polymer is not degraded substantially on exposure to the highly aggressive Cr(VI) solution. Regardless of the concentration of Cr(VI), the composite was restored to 100% of its efficiency by reduction at −945 mV(SCE) in the 0.1 mol dm^{-3} H_2SO_4 solution for a 30-min period. This procedure was repeated three times; the composite was exposed to Cr(VI) for 24 h, then reduced, exposed to a fresh solution of Cr(VI) for a further 24 h, reduced again and finally immersed in a fresh Cr(VI) solution for a further 24 h-period. No loss in the efficiency of the Cr(VI) reduction reaction was seen.

4. Conclusions

The reduction of Cr(VI) by a polypyrrole-modified aluminium electrode proceeds by pseudo-first-order kinetics with an activation energy barrier of 15.13 kJ mol^{-1}. It was found that this catalyst functioned through a regeneration mechanism, whereby Cr(VI) was reduced by PPy^0 to generate PPy$^+$, but the PPy$^+$ was subsequently reduced to PPy^0 by oxidation of the aluminium substrate, thus regeneration of the catalytic PPy^0 surface.

Acknowledgements

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