Polypyrrole electrodeposited on copper from an aqueous phosphate solution: Corrosion protection properties

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Abstract

Highly adherent and homogenous polypyrrole films were electrodeposited at copper from a dihydrogen phosphate solution. The polypyrrole films were electrosynthesized in the overoxidized state by cycling the copper electrode from –0.4 to 1.8 V (SCE) in a pyrrole-containing phosphate solution. The growth of the polypyrrole films was facilitated by the initial oxidation of the copper electrode in the phosphate solution to generate a mixed copper–phosphate, copper oxide or hydroxide layer. This layer was sufficiently protective to inhibit further dissolution of the copper electrode and sufficiently conductive to enable the electropolymerization of pyrrole at the interface, and the generation of an adherent polypyrrole film.

Potentiodynamic polarization measurements, Tafel analyses and open-circuit potential data revealed that the polypyrrole coating effectively protects the copper substrate from corrosion in a chloride solution. However, the corrosion protection properties were reduced with longer immersion times.
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1. Introduction

In recent years there has been much interest in the development and use of conducting polymers as protective coatings against the corrosion of metals and alloys [1]. Polypyrrole (Ppy) is one of the most promising conducting polymers, in this respect, because of its high conductivity, stability and ease of synthesis. In fact several works have appeared [2–13] dealing with the protection of corrosion susceptible metals by electrochemically generated Ppy. However, comparatively few studies have been devoted to the study of copper protection. This is partly due to the difficulty in electropolymerization of the monomer to generate the conducting polymer on an oxidizable metal, such as copper. Due to its low corrosion potential in aqueous media, copper dissolves at the potential necessary to oxidise the monomer. In order to deposit a film of conducting polymer it is necessary to work in a medium with an electrolyte that can protect the copper surface from dissolution without impeding the electropolymerization process.

In our laboratory we have successfully electropolymerized pyrrole at Cu, CuZn and CuNi from a near-neutral sodium oxalate solution [4,6,10]. These films have significant corrosion protection properties in acidified and neutral 0.1 mol dm^{-3} NaCl solution. Cascalheira et al. [5] also reported the formation of strongly adherent polypyrrole coatings on Cu from an aqueous salicylate solution. Hien et al. [12] used oxalic acid as a protective medium while Prissanaroon et al. [13] reported the electropolymerisation of pyrrole on copper in aqueous dodecylbezene sulfonic acid. In addition, Bazzaoui et al. [14] have shown that it is possible to deposit polypyrrole at copper by oxidizing pyrrole in an aqueous sodium tartrate solution.

In this paper the direct electrosynthesis of highly adherent polypyrrole films on copper in an aqueous phosphate solution is reported. The corrosion protective properties of these films were also studied using electrochemical techniques. To the best of our knowledge there are no other reports in the literature detailing polypyrrole electrosynthesis on copper using a phosphate electrolyte.

2. Experimental

Electrodes were prepared from copper (99.99+%) rod bars (3.0 mm in diameter) embedded in epoxy resin in a Teflon holder with electrical contact being achieved by means of a copper wire threaded into the base of the metal sample. The copper surface was polished to a smooth surface finish, using 1200 g SiC, rinsed with acetone and distilled water and dried in air. The aqueous electropolymerization solution was 0.1 mol dm^{-3} pyrrole and 0.1 mol dm^{-3} sodium dihydrogen phosphate at a pH of 4.5. All corrosion tests were performed in a 0.1 mol dm^{-3} NaCl solution, pH 5.5. In order to probe the corrosion reactions under real conditions, the solution was not deoxygenated. All solutions were freely aerated so that the corrosion of copper would not be limited by the absence of dissolved oxygen in the solution.

The surface morphology was recorded by scanning electron microscopy (SEM) with a Jeol model JSM 6400 microscope. Polymer films were peeled back from the copper electrode and glued with graphite paste to a copper holder. Then, they were coated by sputtering with a gold film to avoid charge build-up because of their low conductivity. No metallization effects over morphology of these films have been observed. The uncoated

copper electrodes were rinsed with distilled water to remove any surface chloride, dried and then analysed.

Electrochemical experiments were carried out using a Solartron 1250 frequency response analyser and a Solartron EI 1287 electrochemical interface. A single compartment three electrode cell, with copper as the working electrode, platinum as the counter electrode and a calomel electrode (SCE) as the reference electrode, was employed. The polymers were grown using cyclic voltammetry between –400 and 1800 mV vs SCE at a scan rate of 50 mV s^{-1}.

The corrosion studies were performed at room temperature using the potentiodynamic polarization technique in the chloride-containing solution. The electrode was polarized from below the corrosion potential, at a scan rate of 0.5 mV s^{-1} in the anodic direction, until breakdown occurred. Tafel polarization curves were obtained from –250 mV below the corrosion potential to +250 mV above the corrosion potential at a scan rate of 0.166 mV s^{-1}. The open-circuit potentials of copper and the polypyrrole-coated copper were followed as a function of time. Electrochemical impedance measurements were recorded under open-circuit conditions in 0.1 mol dm^{-3} NaCl for both the copper and polypyrrole-covered copper electrodes. An excitation voltage of 10 mV peak-to-peak was used. The frequency of the potential perturbation was varied between 65 kHz and 2 mHz. All impedance data were fit to appropriate equivalent circuits using a complex non-linear least squares fitting routine, using both the real and imaginary components.

Ex-situ infrared spectra of the polypyrrole films deposited on the copper electrode were recorded at 4 cm^{-1} resolution in a Nicolet Magna 750 FTIR instrument using a Spectra Tech IR-Plan Advantage Microscope.

All electrochemical-based experiments were repeated at least three times. Very good reproducibility was obtained in the growth of the polymer at the copper interface and in the electrochemical polarization studies.

3. Results and discussion

3.1. Electrochemical synthesis

The copper electrodes were first cycled between –0.4 V and 1.8 V in 0.1 mol dm^{-3} sodium dihydrogen phosphate solution to probe the processes which take place at the copper interface in the phosphate solution. Typical cyclic voltammetry data are presented in Fig. 1. The first cycle shows an increase in the anodic current density with applied potentials higher than approximately 0.0 V (SCE) and a broad anodic peak at around 0.9 V (SCE). There is a slight decrease in the anodic current with higher potentials and a considerable decrease in the anodic current on the reverse cycle. These high anodic currents observed in the forward cycle are consistent with the dissolution of copper to generate Cu$^+$ and Cu^{2+} ions (at higher potentials) in solution. However, the voltammograms are very different in the second and particularly the third and subsequent cycles. A considerable decrease in the anodic current density is observed, consistent with passivation of the electrode. The oxidized copper ions complex with the phosphate species to form an insoluble copper phosphate salt, which adheres to the electrode surface protecting copper from further dissolution.

The phosphate species in solution will consist predominantly of H$_2$PO$_4^-$, and to a much lesser extent HPO$_4^{2-}$ and PO$_4^{3-}$. These anions will complex readily with the oxidized copper

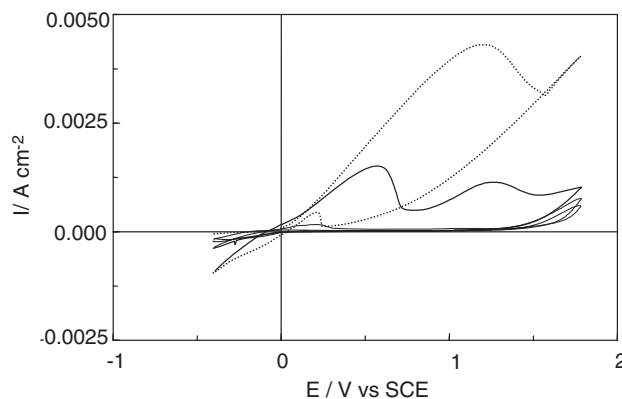Fig. 1. Cyclic voltammograms of copper in aqueous 0.1 mol dm^{-3} NaH$_2$PO$_4$ solution, (···) 1st cycle, (—) 2nd, 3rd and 4th cycles.

cations to form Cu$_3$(PO$_4$)$_2$ which has a low solubility product of 1.40×10^{-37}, through Eqs. (1)–(3).

$$3Cu^{2+} + 2H_2PO_4^- \rightarrow Cu_3(PO_4)_2 + 4H^+ \tag{1}$$

$$3Cu^{2+} + 2HPO_4^{2-} \rightarrow Cu_3(PO_4)_2 + 2H^+ \tag{2}$$

$$3Cu^{2+} + 2PO_4^{3-} \rightarrow Cu_3(PO_4)_2 \tag{3}$$

Accordingly, the passive layer is likely to consist of the highly insoluble Cu$_3$(PO$_4$)$_2$ precipitate, or hydrated precipitate, and copper oxides or hydroxides. Due to the formation of this protective layer, polypyrrole is synthesized on the copper surface when the copper is cycled between –0.4 and 1.8 V (SCE) in a solution of 0.1 mol dm^{-3} NaH$_2$PO$_4$ containing pyrrole. Fig. 2 shows the first and subsequent cycles recorded in the pyrrole solution. It is clear that the presence of pyrrole diminishes the copper dissolution reaction as the anodic
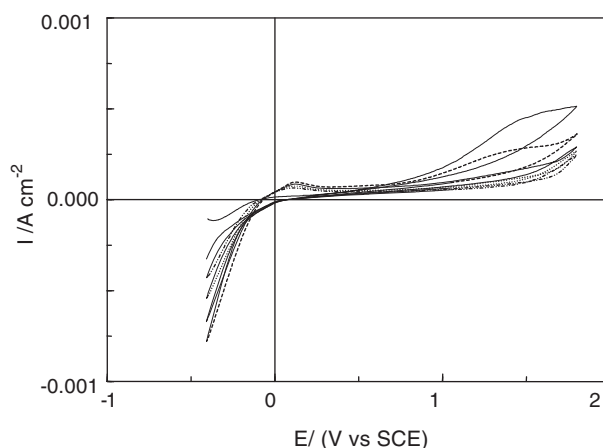

Fig. 2. Cyclic voltammograms of copper in aqueous 0.1 mol dm^{-3} NaH$_2$PO$_4$ and 0.1 mol dm^{-3} pyrrole solution, (—) 1st cycle, (---) 2nd, (—) 3rd, (----) 4th and 5th cycles.

current observed in the first cycle is now considerably lower than that observed in the absence of pyrrole. The anodic current begins to increase at approximately 0.8 V (SCE) which is consistent with the oxidation of the pyrrole monomer [15,16]. A second peak is visible at about 1.3 V (SCE) in the first cycle. This is consistent with the overoxidation of polypyrrole [17,18]. It is also observed that the current decays with successive cycles, with a considerable decrease in the anodic current between the first and second cycles. This electrochemical behaviour is typical of that observed with overoxidized polypyrrole where the increasing resistance and structural changes induced during overoxidation give rise to lower currents [18]. After the 5th cycle a dark film of overoxidized polypyrrole with a smooth surface, which is very adherent to the copper substrate, is observed.

3.2. Surface analysis of deposited Polypyrrole

The SEM micrograph of the electrodeposited polypyrrole film is shown in Fig. 3a, while the FTIR spectrum is shown in Fig. 3b. In both cases, the polymer was formed by cycling the electrode for 5 cycles in the pyrrole-containing solution between –0.4 and 1.8 V (SCE). The SEM micrograph shows the typical characteristic morphology of polypyrrole deposited at inert substrates [19]. The FTIR spectrum shows strong absorption bands at 3340 cm^{-1} due to the N–H stretching mode and at 1633 and 1444 cm^{-1} corresponding to C–C and C–H ring vibrations, and at 1053 and 990 cm^{-1} corresponding to deformation vibrations. Again, these are in good agreement with literature values [20]. It can also be deduced from this analysis that the deposited polypyrrole is overoxidized, the strong absorbance band centred at approximately 1630 cm^{-1} has a slight shoulder peak in the region where the carbonyl absorbs, 1720 cm^{-1}. It is well documented in the literature that the overoxidation of polypyrrole involves hydroxylation and carbonylation reactions and the introduction of carbonyl groups into the polymer backbone structure [21,22].

3.3. Corrosion protection properties

Fig. 4 shows the open-circuit potential variation with time of the copper electrode compared to the polypyrrole-coated copper electrode in a 0.1 mol dm^{-3} NaCl solution. As can
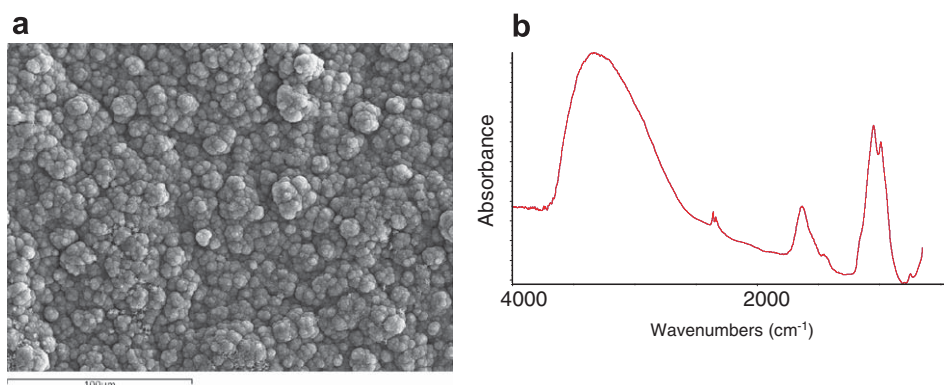

Fig. 3. (a) SEM micrograph of polypyrrole deposited at copper and (b) FTIR spectrum of polypyrrole deposited at copper.
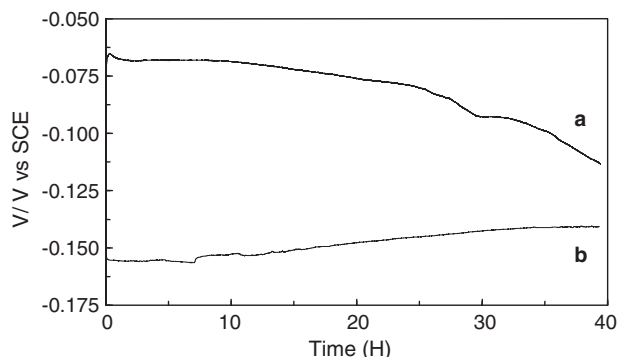
Fig. 4. Open-circuit potential time plot of (a) polypyrrole-coated copper and (b) pure copper in 0.1 mol dm^{-3} NaCl.

be observed the open-circuit potential of the polypyrrole-covered copper is initially much nobler than the untreated electrode under the same conditions. This indicates that the polypyrrole film provides corrosion protective properties. However, after approximately 20 h of immersion, there is a decrease in the open-circuit potential of the polypyrrole-coated electrode and after 40 h of immersion the open-circuit potential is only slightly higher than that recorded for the uncoated copper electrode. This may be due to water intake by the polymer and possibly the transport of chloride anions across the polypyrrole film to the copper interface. However, as the polypyrrole film is irreversibly overoxidized, doping of the polypyrrole by the chloride anions should not occur.

The anodic polarization curves obtained for uncoated and polypyrrole-coated copper electrodes are shown in Fig. 5. Included for comparative purposes is the polarization curve recorded for phosphate-coated copper. The phosphate layer was formed by cycling the copper electrode in the phosphate solution between −0.4 and 1.8 V (SCE) in 0.1 mol dm^{-3} NaH$_2$PO$_4$ for five cycles. The polypyrrole-coated copper substrate has considerably lower current values and a higher corrosion potential than the pure copper. The anodic current
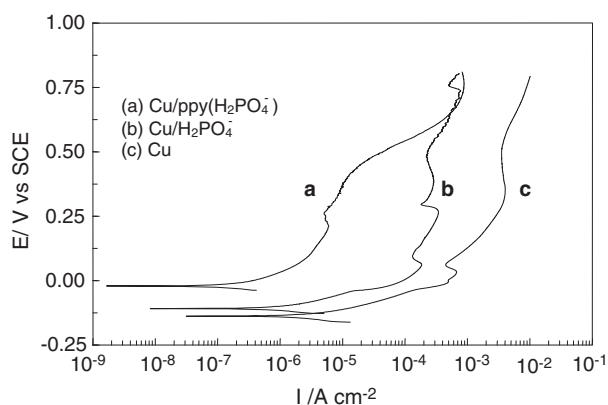

Fig. 5. Potentiodynamic polarization curves recorded at 0.5 mV s^{-1} for (a) polypyrrole-coated copper, (b) phosphate-coated copper and (c) pure copper in 0.1 mol dm^{-3} NaCl.

measured between 0.0 and 0.4 V (SCE) is some two orders of magnitude lower for the polypyrrole-coated electrode compared to the uncoated copper. The trace recorded for the phosphate-coated copper electrode shows clearly that the phosphate layer diminishes the dissolution of copper, but it is also clear from Fig. 5, that the corrosion protection properties are increased further with the deposition of the polypyrrole coating.

From the anodic and cathodic polarization curves (Tafel plots, Fig. 6) the corrosion current density, I_{corr} and corrosion potential, E_{corr}, values were obtained. Linear Tafel regions can be seen clearly in Fig. 6. However, the linear regions are only observed at slow scan rates (0.166 mV s^{-1}); this linearity is lost at higher scan rates of 0.5 mV s^{-1}, as evidenced from Fig. 5. Accordingly, only the lower scan rates were used in the Tafel analyses. Values of these electrochemical parameters and inhibition efficiencies of the polypyrrole are given in Table 1. Inhibiting efficiency is defined in accordance with Eq. (4)

$$I(\%) = (I^\circ_{corr} - I_{corr})/I^\circ_{corr} \times 100 \tag{4}$$

Here, I°_{corr} and I_{corr} are the corrosion currents for the uncoated and coated copper electrodes respectively.

It is clear from Table 1 that there is a reduction in I_{corr} and an increase in E_{corr} on deposition of polypyrrole at copper. The inhibiting efficiency, I (%), is computed as 77.4%. Table 1 also includes data for the polymer-coated copper after 8 days immersion in 0.1 mol dm^{-3} NaCl. After the 8-day immersion it is seen that E_{corr} approaches values similar to that obtained for uncoated copper. However, the I_{corr} value remains relatively low,
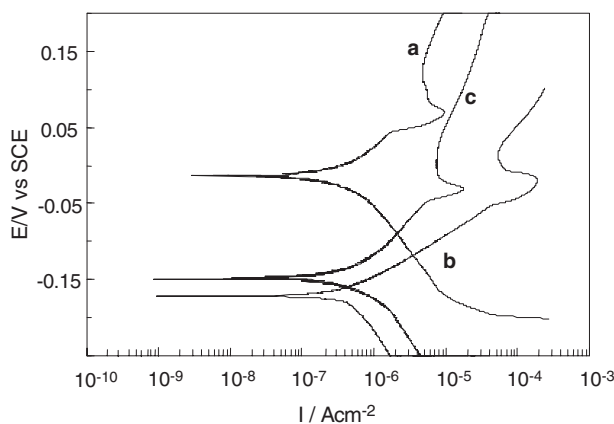

Fig. 6. Tafel curves recorded at 0.166 mV s^{-1} in 0.1 mol dm^{-3} NaCl solution for (a) polypyrrole-coated copper (b) pure copper and (c) polypyrrole-coated copper after 8 days immersion in 0.1 mol dm^{-3} NaCl solution.

Table 1
Corrosion parameters calculated from Tafel plots for pure copper, polypyrrole-coated copper and polypyrrole-coated copper following 8 days immersion in 0.1 mol dm^{-3} NaCl

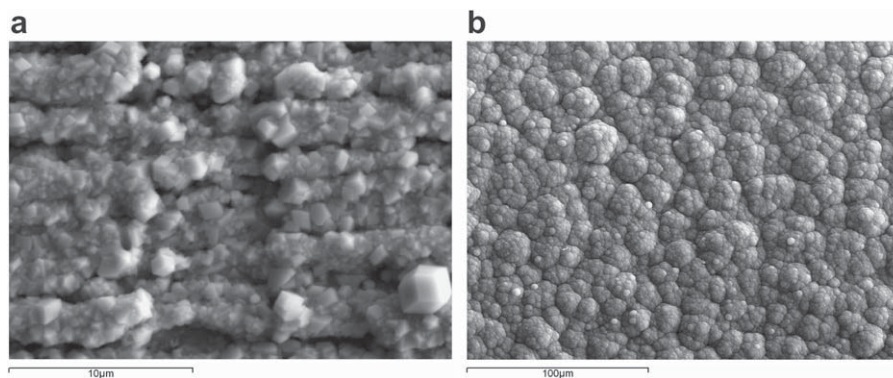| System	$I_{corr}/(\mu A\ cm^{-2})$	$-E_{corr}$ /(mV/SCE)	$-B_c$ /(V dec^{-1})	B_a /(V dec^{-1})	I (%)
Cu	2.94 ± 0.05	172 ± 4	0.17 ± 0.01	0.06 ± 0.01	–
Cu/Ppy	0.66 ± 0.03	14 ± 3	0.14 ± 0.01	0.14 ± 0.01	77.4 ± 4.5
Cu/Ppy (8 days)	1.71 ± 0.10	150 ± 10	0.21 ± 0.02	0.24 ± 0.02	41.9 ± 5.8

Fig. 7. SEM micrograph of (a) pure copper and (b) polypyrrole-coated copper immersed in 0.1 mol dm^{-3} NaCl for 7 days.

which gives an inhibiting efficiency of 41.9%. This result shows that although the corrosive chloride ions diminish the protection properties of the coating the presence of the polymer protects the copper substrate, to some extent, even after 8 days of immersion in the chloride solution.

In Fig. 7, the surface morphology of the uncoated copper and polypyrrole-coated copper electrode following 7 days immersion in the chloride solution are shown. The uncoated copper electrode appears covered by insoluble corrosion products of copper oxides and chlorides, most likely the sparingly-soluble atacamite $(Cu_2(OH)_3Cl)$ [23]. It is well documented that the electrodissolution of copper occurs through the oxidation of Cu to Cu^+, the reaction of Cu^+ with Cl^- to generate CuCl, and the transformation of the CuCl to $CuCl_2^-$. The accompanying reduction reaction is the reduction of dissolved oxygen to generate hydroxyl anions. The sparingly-soluble atacamite is produced from the reaction of the hydroxyl anions and the cuprous chloride [23,24]. The micrograph in Fig. 7a is consistent with the deposition of large amounts of this insoluble corrosion product. Although pitting or micro-pitting may occur initially, the dominating corrosion process is general dissolution in this pH 5.5 solution. As evident from Fig. 7b, these corrosion compounds are not observed on the surface when the copper is coated by polypyrrole. Only the polypyrrole morphology, evident in Fig. 3a, is observed after 7 days of immersion in the corrosive solution. The lack of any localized build-up of corrosion products on the polypyrrole surface indicates that the corrosion is largely uniform at polypyrrole-coated copper and is not initiated at defects or holes in the polypyrrole film.

Interestingly, the corrosion protection properties of the polypyrrole films can be somewhat restored by polarizing the samples in the phosphate solution, as shown in Fig. 8. In this figure three plots are compared, the freshly deposited polypyrrole-coated electrode, the coated electrode following 8 days immersion in 0.1 mol dm^{-3} NaCl and the coated electrode following 8 days immersion in 0.1 mol dm^{-3} NaCl followed by polarization at 50 mV s^{-1} between –0.4 and 1.8 V in 0.1 mol dm^{-3} NaH$_2$PO$_4$ for 20 cycles. It can be seen from Fig. 8 that an increase in the corrosion potential and a reduction in the anodic current is observed on treating the immersed polypyrrole-coated copper in the phosphate solution. The protective properties of the film are somewhat restored and approach that of the freshly synthesized coating. These data show that the phosphate anions play an important role in protecting the copper from corrosion. Although the polymer is irrevers-
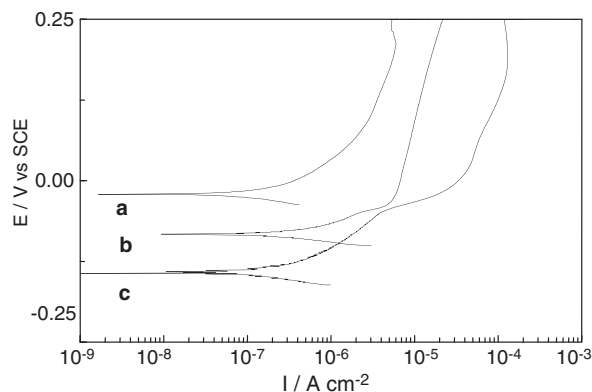
Fig. 8. Potentiodynamic polarization curves recorded at 0.5 mV s^{-1} in 0.1 mol dm^{-3} NaCl for (a) polypyrrole-coated copper, (b) polypyrrole-coated copper following 8 days of immersion in 0.1 mol dm^{-3} NaCl followed by polarization in 0.1 mol dm^{-3} NaH$_2$PO$_4$ between −0.4 and 1.8 V for 20 cycles and (c) polypyrrole-coated copper following 8 days of immersion in 0.1 mol dm^{-3} NaCl.

ibly overoxidized, the phosphate anions are incorporated and transported within the polypyrrole on cycling in the phosphate solution, these anions may then complex with oxidized copper at the copper-polypyrrole interface to generate a Cu$_2$(PO$_4$)$_3$ layer at the interface. It is also interesting to compare the plot recorded for the phosphate-modified pure copper substrate, Fig. 5, with plot (b) in Fig. 8. The phosphate-modified copper has a corrosion potential of approximately –0.12 V (SCE) and an anodic current of 1×10^{-4} A cm^{-2} in the potential interval of 0.0–0.25 V (SCE). The anodic current in the same potential interval is an order of magnitude lower and the corrosion potential is higher for plot (b) in Fig. 8. This suggests that the beneficial effects observed on cycling the polypyrrole-coated copper electrode in the phosphate solution following 8 days of immersion in the chloride solution are not simply due to the deposition of a phosphate layer at the copper polymer interface.

In Fig. 9, the complex plane plots of the polypyrrole-coated copper electrode after 30 min and 7 days immersion in 0.1 mol dm^{-3} NaCl are compared with that of pure copper immersed in the same solution for a 30 min period. These data were recorded under open-circuit conditions. The open-circuit potentials were –170 mV, −10 mV and –130 mV for the pure copper, polypyrrole-coated copper following 30 min immersion and polypyrrole-coated copper following 7 days immersion, respectively. The experimental data are shown as symbols while the simulated data generated using the equivalent circuits depicted in Fig. 9 are shown as the solid traces on the plots. As can be observed these equivalent circuits fit very well to the experimental data.

The data recorded for pure copper immersed in the neutral chloride solution, Fig. 9a, can be fitted to a simple Randles-like circuit. This is an oversimplified model to represent the complex reactions, which take place at the copper interface, but this model has been employed previously [25] and is adequate for the computation of the charge-transfer resistance. In this analysis, R_s represents the solution resistance, R_{CT} corresponds to the charge-transfer resistance and Q_1 is a constant phase element, which in this case has an exponent of 0.45, which represents a diffusion-controlled process. This is consistent with the formation of a passive/corrosion product layer that consists of a mixture of copper oxide/hydroxide and various copper-chloride complexes, which are precipitated at the
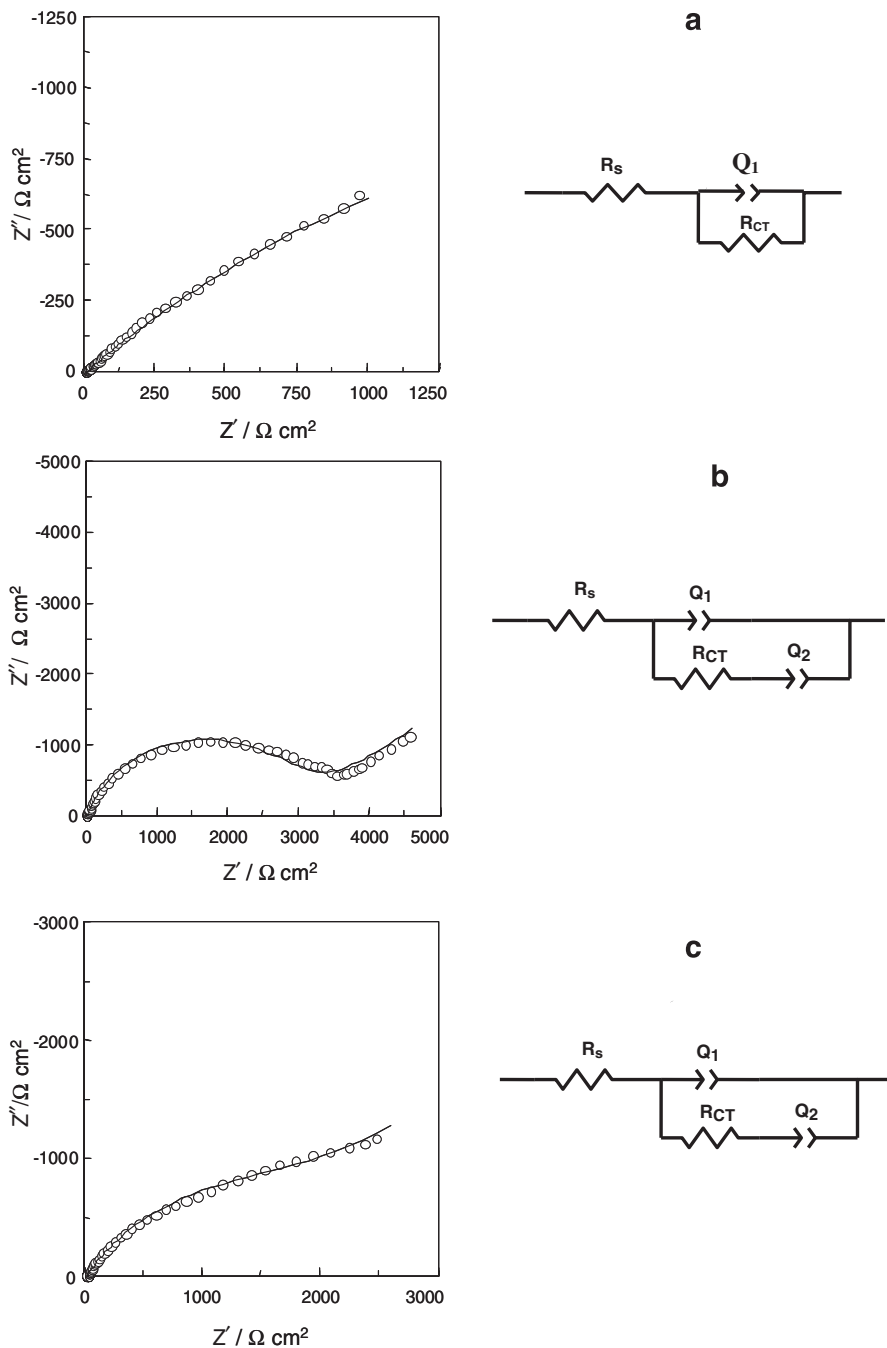
Fig. 9. Complex plane plots recorded in 0.1 mol dm^{-3} NaCl of (a) pure copper after a 30-min immersion period in 0.1 mol dm^{-3} NaCl, (b) polypyrrole-coated copper after a 30 min immersion period in 0.1 mol dm^{-3} NaCl and (c) polypyrrole-coated copper after a 7-day immersion period in 0.1 mol dm^{-3} NaCl.

interface. The charge-transfer resistance computed for pure copper after a 30 min immersion period is 2480 $\Omega\,cm^2$.

The impedance response of the polypyrrole-coated copper immersed for the same period, Fig. 9b is considerably different. The complex plane plot shows a semicircle at high frequencies which can be fitted to an RQ couple, while the data in the low frequency region requires a second constant phase element Q_2 for the fitting routine, Fig. 9b. Q_2 corresponds to the diffusion process with an exponent of 0.45. In this case, Q_1 corresponds to a capacitance term with a value of 3.1×10^{-5} F cm^{-2}, which is equivalent to a double layer capacitance. The charge-transfer resistance, R_{CT}, has a value of 3030 $\Omega\,cm^2$. This is only slightly higher than the R_{CT} value computed for pure copper. However, the R_{CT} value computed for pure copper is dominated by the insoluble corrosion products, which limit the electrodissolution of the copper. Interestingly, both the Q_1 and R_{CT} values are consistent with an oxidized polypyrrole film, which is not conducting and consequently, the polypyrrole film will act only as a barrier coating.

In Fig. 9c the impedance response of the polypyrrole-coated copper after a 7 day immersion period is shown. These data were fit to the equivalent circuit depicted in Fig. 9c where again Q_2 represents a diffusion term. The R_{CT} value is 2440 $\Omega\,cm^2$ which is lower than that observed after 30 min immersion, indicating a loss in the barrier protection property of the polypyrrole film. This decrease in the R_{CT} value is in agreement with the corrosion data presented in Table 1.

4. Conclusions

It is shown that polypyrrole can be electrodeposited directly on a copper substrate using NaH$_2$PO$_4$ aqueous solution. The polymer obtained is uniform, compact and strongly adherent to the copper substrate. The variation of the open-circuit potential with time, Tafel analyses and potentiodynamic polarization studies reveal that the coating protects the copper from corrosion. The overoxidized polypyrrole coating acts as a physical barrier to corrosion. The intake of chloride ions diminishes the inhibiting efficiency of the polymer. However, the inhibiting effect remains even after 8 days of continuous immersion in 0.1 mol dm^{-3} NaCl.

Acknowledgements

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