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The electropolymerization of pyrrole at a CuNi electrode: corrosion protection properties

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Abstract

Pyrrole was successfully electropolymerized at a copper–nickel electrode in a near-neutral sodium oxalate solution containing Cu^{2+} cations to generate a homogenous and adherent polypyrrole film. The presence of the Cu^{2+} ions increased both the rate of the electropolymerization reaction and the adherence of the polymer at the CuNi interface. In the absence of these cations, oxidation of the electrode occurred generating a nickel-rich layer that was not sufficiently conducting, under the electropolymerization conditions employed, to facilitate the electron-transfer reaction and the electropolymerization of pyrrole.

These films remained stable and exhibited significant corrosion protection properties in acidified and neutral 0.1 mol dm^{-3} NaCl solutions even on polarization of the electrodes to high anodic potentials.

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1. Introduction

It is well known that the addition of nickel to copper, as an alloying component, to form CuNi alloys, gives rise to the production of a corrosion resistant material [1–3]. CuNi alloys, particularly the commercial 70Cu30Ni, exhibit good resistance to generalized and localized corrosion and consequently find applications, such as in the production of heat exchangers, in many different industries. Nevertheless, there is

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much interest in developing corrosion protection strategies to increase further the corrosion resistance of these alloys.

Many of the corrosion protection strategies centre on the inhibitors employed in the corrosion protection of pure copper. For example, the well-known benzotriazole species, which is an excellent corrosion inhibitor for pure copper [4–6], has been used to inhibit the electrodisolution of Cu–10Ni [7]. There are also a number of reports detailing the corrosion protection of copper and copper nickel alloys using organic compounds, such as propargyl alcohol, aminotriazole and various Schiff bases [8–13].

Although conducting polymers have been used extensively in the corrosion protection of iron and iron-based alloys [14–17] there are very few reports devoted to the corrosion protection properties of these polymers when applied to copper or copper-based alloys. There is only one report detailing the direct electropolymerization of pyrrole to form adherent polypyrrole at pure copper [18]. In all other cases, where these polymers have been considered, they have first been synthesized chemically, and then deposited at the metal surface, by spin coating [19]. For example, Brusic et al. [19] have studied the corrosion protection properties of polyaniline and its derivatives when spin-coated onto copper as a function of the applied potential and temperature. It was found that polyaniline could either enhance the corrosion rate or produce significant corrosion protection properties depending on the chemical nature of the polymer backbone and on the oxidation state and extent and nature of polymer doping.

In this paper results are presented on the electropolymerization of pyrrole at a copper–nickel electrode from a near-neutral oxalate solution containing copper cations to produce an adherent polypyrrole coating. The corrosion protection properties of this layer are assessed using electrochemical techniques. To the best of our knowledge there are no reports in the literature concerning the electropolymerization of pyrrole at a copper–nickel surface to generate adherent polypyrrole layers which exhibit corrosion protection properties.

2. Experimental

Electrodes were prepared from pure copper (99.99+%) and a 70Cu30Ni alloy. The electrodes were provided in rod form (5 mm in diameter). These rods were embedded in epoxy resin in a Teflon holder. A copper wire was threaded into the base of the sample to provide electrical contact. Prior to each test the exposed surfaces were polished to a smooth surface finish, using 1200 g SiC, and rinsed with distilled water. A standard three-electrode cell was used as the electrochemical cell. High-density graphite rods were used as the auxiliary electrodes and a saturated calomel electrode (SCE) was used as the reference electrode. The electrolytes were prepared using analytical grade reagents and distilled water.

The electropolymerization solution consisted of 0.1 or 0.2 mol dm⁻³ pyrrole and a 0.125 mol dm⁻³ sodium oxalate solution maintained at a pH of 7.6. Cu²⁺ cations, in the concentration range of 1.0 × 10⁻³ to 1.0 × 10⁻² mol dm⁻³, were added to the

electropolymerization solution as CuSO_4 . A 0.001 or 0.01 mol dm^{-3} CuSO_4 solution was used to deposit a copper layer at the CuNi electrode using a deposition potential of -0.4 V(SCE) for periods of 5 min. A 0.1 mol dm^{-3} NaCl solution, adjusted to pH values of 3.5 and 7.8, using either NaOH or HCl was used as the aggressive solution. Electrochemical experiments were carried out using an EG&G Potentiostat, Model 263, or a Solartron EI 1287 electrochemical interface. The polymers were formed using a constant potential of 900 mV(SCE).

Once formed, the electrochemical and corrosion protection properties of the polymer-modified electrodes were assessed. The electrochemical tests consisted of cyclic voltammetry, while the corrosion tests involved anodic polarization measurements. Cyclic voltammograms were recorded in the monomer-free oxalate solution at 20 mV s^{-1} from an initial potential of -500 mV(SCE) up to a vertex potential of 1000 mV(SCE). Anodic polarization tests were recorded in the chloride-containing solutions from below the corrosion potential, at a scan rate of 0.5 mV s^{-1} in the anodic direction, until breakdown occurred.

Scanning electron micrographs were recorded on a Hitachi S-4700 cold cathode field emission SEM using a secondary electron detector and at an accelerating voltage of 15 kV. The samples were gold coated prior to imaging using an Emitech K550 sputter coater.

3. Results and discussion

3.1. Formation of polypyrrole at CuNi

In an earlier paper [18] we have shown that it is possible to electropolymerize pyrrole from a near-neutral oxalate solution at a copper electrode and to generate a homogenous and adherent polypyrrole coating at the copper surface. These polymers could be grown relatively easily using either a potentiostatic or cyclic voltammetric technique. However, growth of polypyrrole at CuNi electrodes is significantly more difficult. In fact, polymer layers could only be grown on CuNi in the $0.125 \text{ mol dm}^{-3}$ sodium oxalate solution at a constant potential of 0.9 V(SCE) using a very high pyrrole concentration of 0.3 mol dm^{-3} . However, this method, which leads to a very high rate of electropolymerization, gave rise to very thick and non-adherent polymers. Pyrrole concentrations lower than this did not lead to reproducible uniform polymer deposition.

This difference between the ease of electropolymerization at copper and the copper nickel electrode seems to be connected with the passive layer that forms on CuNi, which consists of an inner oxide layer and an outer nickel-rich hydroxide layer. Strehblow and co-workers [2,3] have described this layer as a bilayer with a predominately Ni-rich outer hydroxide and a Cu-rich inner oxide. It appears that the presence of this Ni-rich outer layer inhibits the electropolymerization process.

The formation of this relatively stable nickel-rich oxide/hydroxide layer in the oxalate solution can be seen from the data presented in Fig. 1(a), which shows cyclic voltammograms recorded for CuNi in $0.125 \text{ mol dm}^{-3}$ sodium oxalate. For

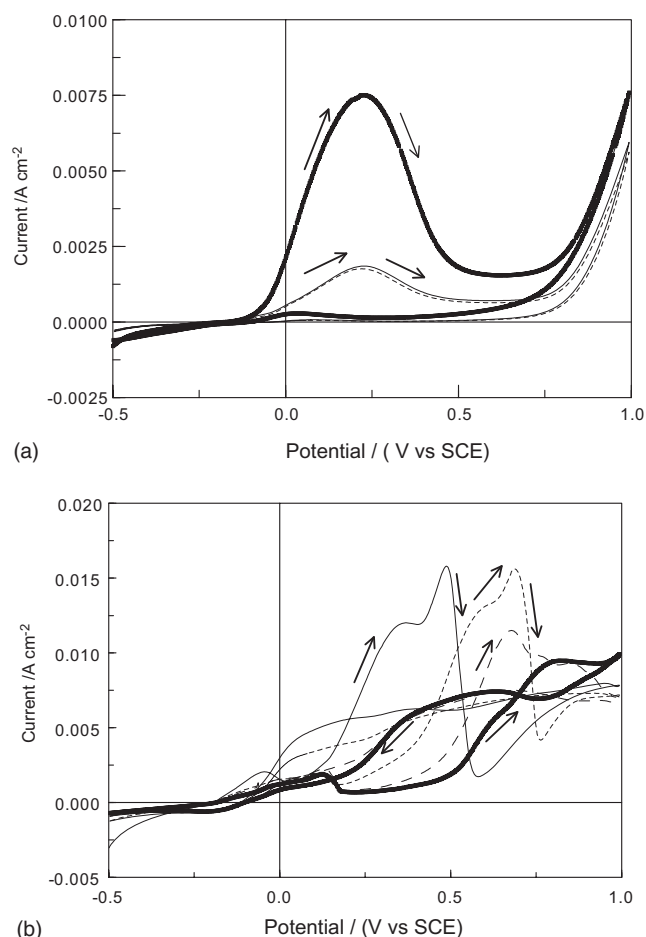


Fig. 1. (a) Cyclic voltammograms recorded for CuNi in $0.125 \text{ mol dm}^{-3} \text{ Na}_2\text{C}_2\text{O}_4$, pH 7.8 solution, (■ ■ ■) 1st cycle, (—) 5th cycle, (---) 9th cycle. (b) Cyclic voltammograms recorded for pure copper in a $0.125 \text{ mol dm}^{-3} \text{ Na}_2\text{C}_2\text{O}_4$, pH 7.8 solution, (—) 1st cycle, (---) 2nd cycle, (- - -) 3rd cycle and (● ● ●) 4th cycle.

comparative purposes, the cyclic voltammograms recorded for pure copper under similar conditions are shown in Fig. 1(b). These data were recorded by polarizing the electrodes from -500 mV(SCE) up to the vertex potential of 1000 mV(SCE) . As evident from a comparison of the two sets of data, the electrochemical behaviour of the Cu and CuNi in the oxalate medium is very different. In the case of the CuNi system, a high current peak is visible at 0.225 V(SCE) in the first cycle, on polarization in the forward direction. This corresponds to the oxidation of the CuNi surface and the subsequent current decay at approximately 500 mV(SCE) may indicate the formation of a stable oxide or hydrated oxide layer enriched in nickel. This anodic current peak is considerably reduced on successive cycling indicating that the nickel-

rich passive layer has protective properties. The cyclic voltammograms recorded for pure copper are very different. In the first cycle, dissolution of copper is seen to begin at -180 mV(SCE), a peak is evident at approximately -40 mV(SCE) which is consistent with the formation of Cu(I) oxide. On polarizing further in the anodic direction, more intense dissolution is seen with current peaks being observed at approximately 360 and 490 mV(SCE). These appear to be connected with the formation of Cu(II) oxalates, with the likely oxalates being Cu(Ox) and Cu(Ox)_2^{2-} , where Ox represents the oxalate species [18,20]. On the second and subsequent cycles, the potential at which these reactions occur increases in the anodic direction which suggests some stabilization of the copper electrode as a result of the formation of copper-oxalate corrosion products on the surface.

Even though, the electrochemical behaviour of pure copper appears more complex than that of the CuNi electrode, it was possible to deposit polypyrrole at pure copper using this cyclic electrolysis technique [18], whereas there was no evidence of any polypyrrole formation at the CuNi electrode. Changing the potential limits, scan rate or concentrations of monomer had little beneficial effects. This is not surprising, since it is well known that Ni(OH)_2 is stable and cannot be reduced at potentials higher than -0.5 V(SHE) [2]. Secondly, the application of high potentials, which are needed to initiate the electropolymerization reactions, also give rise to increased rates of the formation of the nickel hydroxide. It appears under the experimental conditions used here that the nickel-rich oxide layer that is formed during oxidation of the CuNi alloy is not sufficiently conductive to enable electron transfer and the electropolymerization reaction. Nevertheless, there are reports detailing the electropolymerization of pyrrole at a pure nickel substrate. For example, Zalewska et al. [21] have deposited polypyrrole at nickel from an acetonitrile solution. XPS analysis of the polymer revealed the presence of Ni^{2+} chemically bound to the polymer chain, indicating dissolution of the substrate during the electropolymerization reaction.

However, it was possible to deposit adherent and homogenous polypyrrole coatings at CuNi by adding Cu^{2+} ions to the electropolymerization solution. Representative plots are shown in Fig. 2, which illustrate the effect of varying the CuSO_4 concentration on the rate of polymer formation. A very high rate of electropolymerization is evident with the higher $0.01 \text{ mol dm}^{-3} \text{ Cu}^{2+}$. The current rises and continues to increase leading to the production of a very thick, but highly adherent polymer. On reducing the concentration of CuSO_4 to that of $0.001 \text{ mol dm}^{-3}$, there is a considerable reduction in the anodic current and consequently the rate of electropolymerization. But, again this procedure leads to the production of adherent polypyrrole coatings at the CuNi surface.

It was possible also to control the electropolymerization process by first depositing a thin layer of Cu onto the CuNi electrode prior to electropolymerization. This was achieved by depositing copper from a $0.001 \text{ mol dm}^{-3} \text{ CuSO}_4$ solution, or in some experiments from a $0.01 \text{ mol dm}^{-3} \text{ CuSO}_4$ solution, at a potential of -0.4 V(SCE) for 5 min. Data showing the influence of the pyrrole concentration and copper cation concentration on the charge passed during the electropolymerization process at this copper-modified electrode are shown in Fig. 3. Although there is some variation between identical experiments, the reproducibility of the charge passed during the

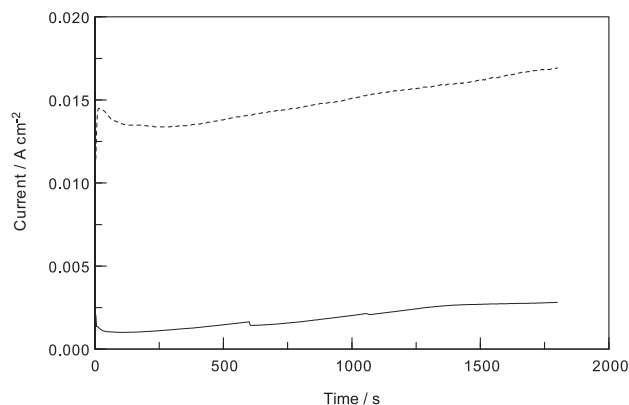


Fig. 2. Potentiostatic current–time plots for CuNi in $0.125 \text{ mol dm}^{-3} \text{ Na}_2\text{C}_2\text{O}_4$, and 0.2 mol dm^{-3} pyrrole (---) in the presence of $0.01 \text{ mol dm}^{-3} \text{ CuSO}_4$ and (—) in the presence of $0.001 \text{ mol dm}^{-3} \text{ CuSO}_4$.

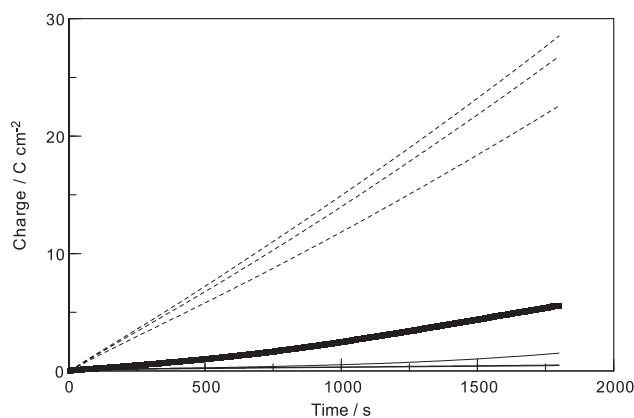
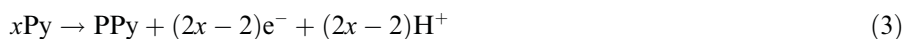
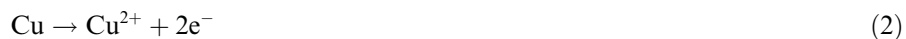


Fig. 3. Charge–time plots recorded for a copper-modified CuNi electrode in $0.125 \text{ mol dm}^{-3} \text{ Na}_2\text{C}_2\text{O}_4$ containing (---) 0.2 mol dm^{-3} pyrrole and $0.01 \text{ mol dm}^{-3} \text{ CuSO}_4$, (—) 0.1 mol dm^{-3} pyrrole and $0.01 \text{ mol dm}^{-3} \text{ CuSO}_4$ and (■ ■ ■) 0.2 mol dm^{-3} pyrrole.

early stages of electropolymerization is good. Also, it can be seen that on increasing the monomer concentration, an increase in the charge occurs, indicating a higher rate of electropolymerization, as expected, while higher rates of electropolymerization are observed with higher concentrations of Cu^{2+} . It is also interesting to note that the electropolymerization process proceeds with ease in the absence of dissolved Cu^{2+} provided the surface is modified with a copper layer prior to electropolymerization. As can be seen from these charge–time plots, the charges calculated are very high. These charges comprise elements of substrate dissolution, dissolution of the copper deposited layer, deposition of polypyrrole and oxidation of the polypyrrole, Eqs. (1)–(4).



Therefore, the polypyrrole coatings are likely to contain Cu^{2+} or oxides of copper. Indeed, copper could be detected in the polymer layer using energy dispersive X-ray analysis of a film removed from the substrate. Nevertheless, these procedures lead to the growth of smooth, homogenous and adherent polymer layers on the CuNi surface in a reproducible manner.

Evidence of this can be seen in the SEM image shown in Fig. 4, which shows an adherent crack-free polypyrrole layer on the CuNi surface. These data were recorded following 14 days dehydration after polymerization of 0.2 mol dm^{-3} pyrrole from $0.125 \text{ mol dm}^{-3}$ sodium oxalate solution at a copper deposited CuNi electrode. The surface morphology shows characteristic microspheroidal aggregates of polypyrrole varying in size up to $2.5 \mu\text{m}$. These results agree well with those presented in earlier works where polypyrrole was deposited on pure copper in a similar manner [18].

The increase in polymer growth in the presence of copper cations is evident on comparing the traces recorded in 0.2 mol dm^{-3} pyrrole in the presence and absence of CuSO_4 shown in Fig. 3. This effect has been documented previously by Millar et al. [22]. These authors have shown that the presence of copper cations promotes oxidation of the polymer units during the polymerization process due to the strong oxidizing power of the Cu^{2+} cation. Indeed, these researchers have shown, using PAIR spectroscopy, the presence of vibrations, which have been ascribed to the oxidized form of polypyrrole, proving the existence of the Cu^{2+} induced oxidation

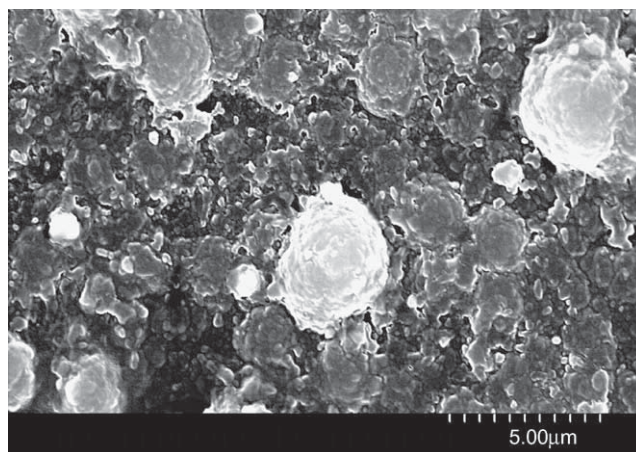


Fig. 4. SEM micrograph of polypyrrole-coated CuNi under high magnification.

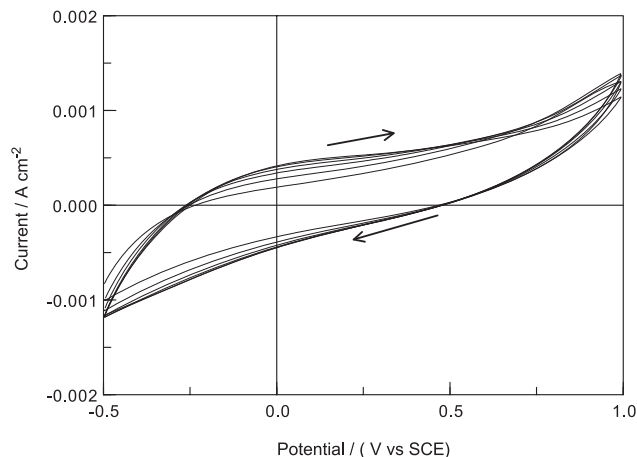


Fig. 5. Successive cyclic voltammograms recorded for a polypyrrole-coated CuNi electrode in $0.125 \text{ mol dm}^{-3} \text{ Na}_2\text{C}_2\text{O}_4$, pH 7.8 solution.

reactions. Rivas and Sanchez [23] have also reported an increase in the polymer yield in the presence of copper cations. However, it is also interesting to note that under the electropolymerization conditions used here that the presence of the Cu^{2+} cations leads to an increase in the adherence of the polypyrrole at the electrode surface.

The cyclic voltammograms recorded for polypyrrole-coated CuNi cycled in the monomer-free $0.125 \text{ mol dm}^{-3} \text{ Na}_2\text{C}_2\text{O}_4$ are presented in Fig. 5. These voltammograms are characteristic of pure polypyrrole. They consist of no visible oxidation or reduction peaks and have a current associated with the conductivity of the polymer film. The current decreases slightly with successive cycling which is consistent with degradation and overoxidation of the polypyrrole on exposure to high anodic potentials in the region of 1.0 V(SCE) [24]. However, it is clear that these polymers inhibit the dissolution of the underlying substrate even though they are polarized to relatively high anodic potentials. There is no evidence of any oxidation peaks as observed for the bare CuNi electrode, Fig. 1, indicating that the polymer prevents the oxidation of the Cu or Ni from the substrate.

3.2. Corrosion protection properties

In order to investigate the corrosion protection properties of the polypyrrole film, uncoated CuNi and coated CuNi were polarized in an aggressive test solution and the results compared. The test solutions consisted of $0.1 \text{ mol dm}^{-3} \text{ NaCl}$ pH 7.8 and a more aggressive pH 3.5 solution. In all these corrosion measurements, the polymers were deposited from 0.2 mol dm^{-3} pyrrole in $0.125 \text{ mol dm}^{-3} \text{ Na}_2\text{C}_2\text{O}_4$ containing $0.001 \text{ mol dm}^{-3} \text{ CuSO}_4$, at a constant potential of 0.9 V(SCE) , following Cu deposition at the CuNi electrode at -0.4 V(SCE) . An approximate film thickness, of $6 \mu\text{m}$, was calculated for these polymers based on the assumption that a charge of

100 mC cm^{-2} is required to form a $0.28 \mu\text{m}$ thick film of polypyrrole [25]. In these analyses the charge computed for polarization of the CuNi electrode in the absence of the monomer was subtracted from the charge passed during the electropolymerization period in an attempt to account for the charge associated with the dissolution reactions, Eqs. (1) and (2). Typical anodic polarization plots recorded for the polypyrrole-coated CuNi electrode and uncoated CuNi in 0.1 mol dm^{-3} NaCl, pH 7.8 and pH 3.5 solutions are shown in Fig. 6(a) and (b) respectively. The current–potential profiles recorded for the uncoated electrodes are consistent with breakdown and dissolution of the electrodes. High anodic currents, in the region of 1 mA cm^{-2} are reached at relatively low potentials. For example, the current exceeds

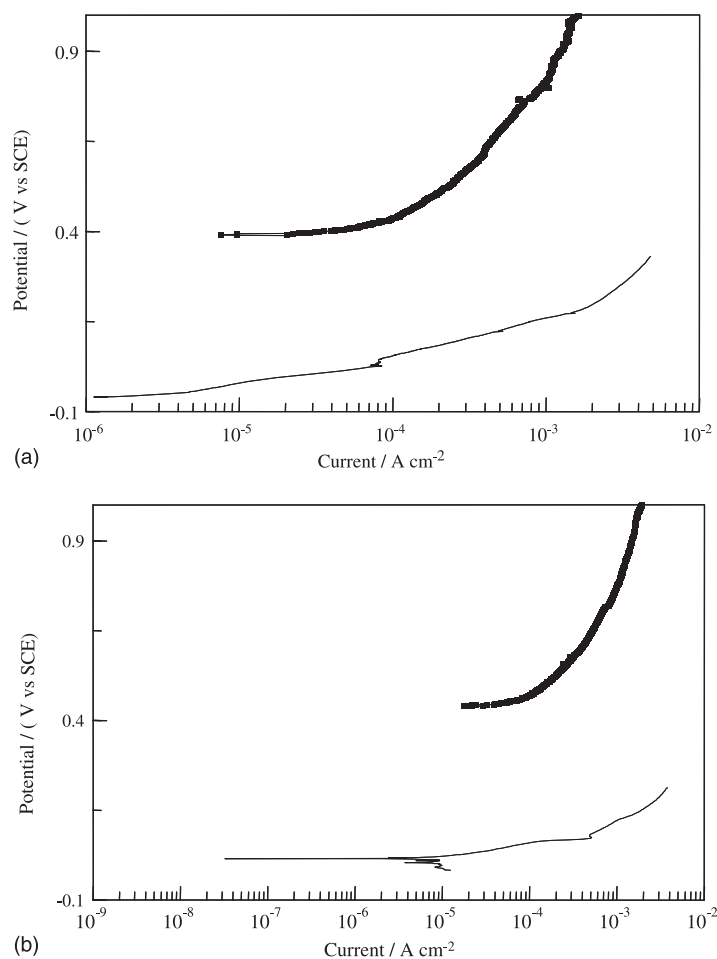


Fig. 6. (a) Anodic polarization plots recorded in a pH 7.8, 0.1 mol dm^{-3} NaCl solution for (●●●) polypyrrole-coated CuNi and (—) uncoated CuNi. (b) Anodic polarization plots recorded in a pH 3.5, 0.1 mol dm^{-3} NaCl solution for (●●●) polypyrrole-coated CuNi and (—) uncoated CuNi.

1 mA cm⁻² at potentials close to 160 mV(SCE) for the uncoated electrode in the near-neutral solution. However, very different behaviour is seen with the polymer-coated substrates. In the case of the neutral solution, the corrosion potential for the polypyrrole-coated electrode is approximately 450 mV more noble than that of the uncoated CuNi electrode, while the potential can be increased to values in excess of 800 mV(SCE) before the anodic current reaches a 1 mA cm⁻² level. A similar increase in the corrosion protection properties is evident in the more aggressive acidic solution. The corrosion potential is increased by almost 400 mV and the potential at which the current adopts a 1 mA cm⁻² value, by over 650 mV compared to the uncoated electrode.

In order to investigate the corrosion protection properties further and the stability of the conducting polymer, the corrosion potentials adopted by the electrodes and the anodic polarization behaviours were recorded as a function of the immersion period in the aggressive chloride-containing solution. The open-circuit potentials recorded as a function of time for polypyrrole-coated CuNi, uncoated CuNi and Cu deposited CuNi in 0.1 mol dm⁻³ NaCl solutions adjusted to a pH of 7.8 and 3.5 are shown in Fig. 7(a) and (b) respectively. In the case of the near-neutral chloride solution the open-circuit potential adopted by the polypyrrole-coated electrode initially reaches values close to 500 mV(SCE) and then decays slowly to reach a near-steady-state value that is some 180 mV higher than that adopted by the uncoated electrode. The open-circuit potential adopted by the copper-modified CuNi electrode is much lower, approximately 130 mV below that adopted by the pure uncoated CuNi electrode, consistent with the higher corrosion rate of the pure copper surface.

This ennoblement in the open-circuit potentials adopted by the polymer-coated electrode has been reported previously for polypyrrole-coated copper [18] polymer-coated aluminium [26] and polyaniline-coated iron electrodes [27]. In the case of the iron systems the corrosion protection properties are often gauged by measuring the period elapsed until the open-circuit potential of the polymer-coated electrode drops to that of the uncoated electrode. This signifies loss of corrosion protection and typically lasts from minutes to hours. However, this is not seen for this CuNi system or indeed for pure copper [18]. Instead, the open-circuit potential remains constant at these near-steady-state values.

It can be seen from the data recorded in the acidic solution, presented in Fig. 7(b), that the open-circuit potentials become near-constant shortly following immersion, and that the highest steady-state potential is recorded for the uncoated CuNi electrode. This is very different to the variations in the open-circuit potentials recorded in Fig. 7(a). However, this seems to be associated with the formation of a copper layer over the electrode prior to electropolymerization. On comparing the open-circuit potential adopted by the polypyrrole-coated electrode with that of the Cu coated CuNi electrode an increase of almost 150 mV is visible for the polypyrrole-coated system. A closer examination of both the acidic and neutral results shows that it is the open-circuit potential of the polypyrrole-coated electrode that changes most on varying the solution pH. Bernard et al. [27] have shown that a drop in the corrosion potential of polyaniline-coated iron, to more electronegative values, corresponds to a loss of the corrosion protection by the polymer. In the case of the copper–nickel

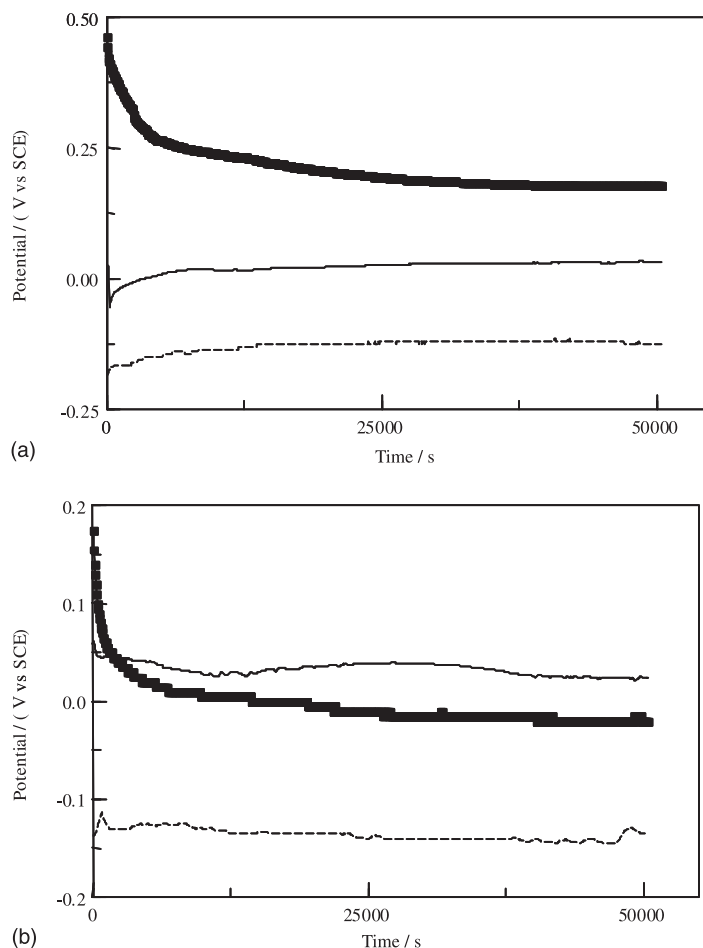


Fig. 7. (a) Open-circuit potential–time plots recorded in a pH 7.8, 0.1 mol dm⁻³ NaCl solution for (●●●) polypyrrole-coated CuNi, (—) uncoated CuNi and (---) Cu deposited CuNi. (b) Open-circuit potential–time plots recorded in a pH 3.5, 0.1 mol dm⁻³ NaCl solution for (●●●) polypyrrole-coated CuNi, (—) uncoated CuNi and (---) Cu deposited CuNi.

electrodes a gradual decay in the open-circuit potential to near 200 mV/SCE is seen in the neutral solution however, a much sharper decrease in the potential is seen to values close to -50 mV/SCE in the acidic solution. This may indicate a change in the protective properties of the polymer in the acidic solution.

The anodic polarization behaviours of these three systems following a 14-h immersion period are shown in Fig. 8(a) and (b) in the neutral and acidified solutions respectively. The copper-modified CuNi electrode appears to be more active than the unmodified CuNi electrode. This is consistent with the passivating properties of the nickel alloying addition [1–3]. It can be seen that the polymer-coated CuNi electrode

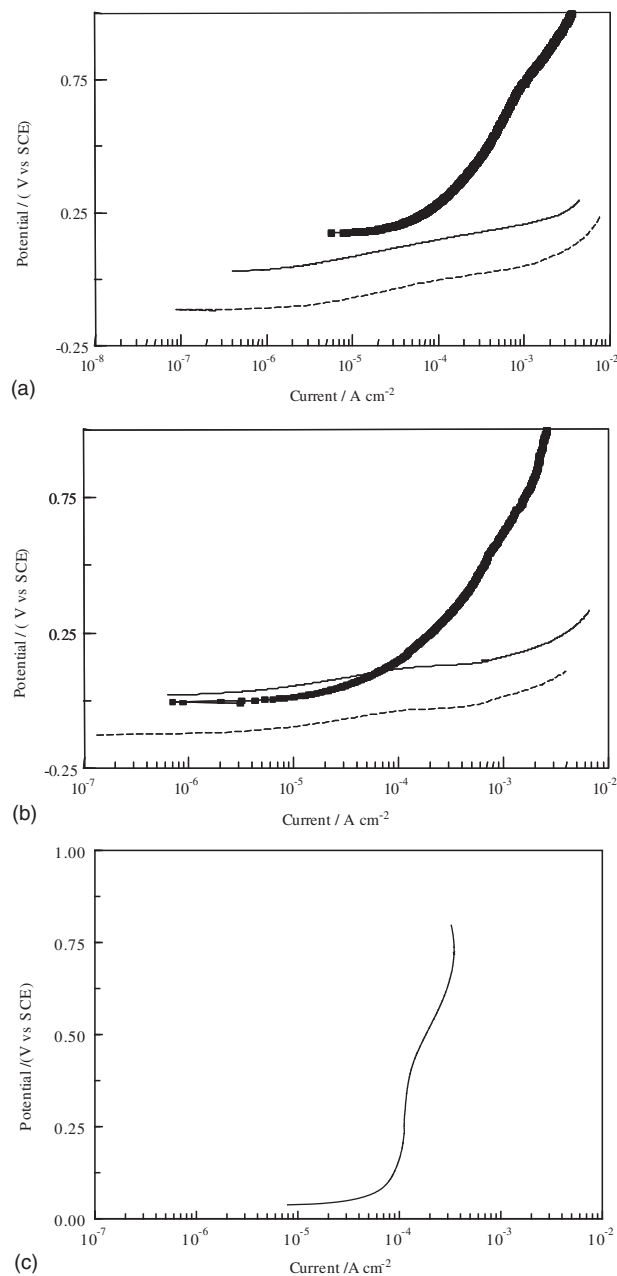


Fig. 8. (a) Anodic polarization plots recorded in a pH 7.8, 0.1 mol dm⁻³ NaCl solution following 14-h immersion for (●●●) polypyrrole-coated CuNi, (—) uncoated CuNi and (---) Cu deposited CuNi. (b) Anodic polarization plots recorded in a pH 3.5, 0.1 mol dm⁻³ NaCl solution following a 14-h immersion period for (●●●) polypyrrole-coated CuNi, (—) uncoated CuNi and (---) Cu deposited CuNi. (c) Anodic polarization plots recorded in a pH 3.5, 0.1 mol dm⁻³ NaCl solution for a polypyrrole-coated platinum electrode.

can be polarized to relatively high anodic potentials before high anodic currents are measured. Indeed, some of the anodic current measured for these polymer-coated electrodes is due to the electroactivity and oxidation of the polypyrrole and not due to dissolution of the substrate. This can be seen by the data presented in Fig. 8(c), which show the anodic polarization behaviour of a polypyrrole-coated platinum electrode in the acidic chloride solution. For example, the anodic current measured at the polypyrrole-coated platinum electrode in the acidic medium reaches values of 0.3 mA cm^{-2} at 500 mV(SCE) , which are close to the values of 0.6 mA cm^{-2} adopted by the polypyrrole-coated CuNi electrode at the same potential, Fig. 8(b). This is even more significant given the fact that the polypyrrole formed at the platinum electrode is a much thinner coating and accordingly will have a lower oxidation current. Possibly the most significant aspect of these data is the fact that the polymer-coated electrodes, despite being immersed in the aggressive solutions for a 14-h period, offer protection to the underlying CuNi electrode. It is also interesting to note that although the open-circuit potentials adopted by the polypyrrole-coated electrode are lower than those measured for the uncoated electrode in the acidic solutions, this polymer continues to exhibit corrosion protection properties on polarization of the electrode in the aggressive solutions.

4. Conclusions

Pyrrole was successfully electropolymerized at a CuNi electrode in a near-neutral sodium oxalate solution containing Cu^{2+} to generate a homogenous and adherent polypyrrole film. The electropolymerization reaction was facilitated by the presence of the copper cations. Indeed, in the absence of these copper cations, it was not possible to form an adherent polypyrrole coating at the CuNi electrode. It appeared that the nickel-rich layer was not sufficiently conducting under the electropolymerization conditions employed to facilitate the electron-transfer reaction and the electropolymerization of pyrrole. These films exhibited significant corrosion protection properties on polarization in acidified and neutral 0.1 mol dm^{-3} NaCl solutions.

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