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Evaluation of the corrosion protection behaviour of poly(neutral red) films on passivated copper

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ABSTRACT

The corrosion protection behaviour of poly(neutral red) (PNR) films on copper electrodes has been investigated using open circuit measurements, Tafel plots and electrochemical impedance spectroscopy. Pure copper electrodes were initially passivated in sodium oxalate, salicylate or hydrogen carbonate solution, to inhibit copper dissolution at potentials where neutral red monomer oxidation occurs, before its electropolymerization by potential cycling. The corrosion inhibition by these films was tested in 0.10 M KCl solution. It was found that, after long immersion times (96 h), the best protection efficiency was with PNR films formed on copper passivated in oxalate solution.

1. Introduction

The oxidation and reduction behaviour of copper has been extensively studied by electrochemical techniques in neutral and alkaline media [1–4]. This interest in the electrochemical characteristics of copper is attributed to its wide range of applications. Although the influence of atmosphere and many chemicals can be negligible, in aggressive media copper is susceptible to corrosion since no protective passive layer is formed on its surface. Numerous copper corrosion inhibitors have been investigated, mainly organic compounds and their derivatives such as azoles, amines and amino acids, e.g. [5].

The best way to promote corrosion protection of metals consists in the application of coatings on the metal formed from inorganic or organic materials. The use of conducting polymers to form in situ films is attracting considerable attention for the corrosion protection of oxidizable metals [6].

However, a major drawback regarding in situ electropolymerization to form conducting polymer coatings on oxidizable metals is that monomer oxidation occurs at higher potentials than that of the dissolution of the metals. For this reason, it is necessary to create a passive layer on the metal surface prior to polymer deposition. Passivation of copper has been carried out in various media, including salicylate, carbonate and oxalate [4,7–12].

Salicylate anions are known to form stable complexes with most transition metals, in particular, in aqueous solution, different soluble complexes of Cu(II) and salicylate. There is thus a strong influence of salicylate ions on the electrochemical behaviour of copper surfaces and on the passivation process [4,7].

Regarding passivation solutions containing carbonate and hydrogen carbonate, the stability of the passive films formed on copper has been found to depend on pH, carbonate–hydrogen carbonate concentration ratio, and hydrodynamics [10]. It has been proposed that the passivation coating on the metal contains layers in which basic copper carbonates precipitate, without interfering appreciably with the formation of copper oxides [9].

In the case of passivation of copper in oxalate solution the passive layer is formed by copper oxides and copper oxalate, which are insoluble in water [12].

Polyphenazines are very attractive redox polymers acting both as conducting polymers and redox mediators. Neutral red (NR; N^8,N^8,3-trimethylphenazine-2,8,-diamine), Fig. 1, is an acid base indicator with p$K_a \sim 6.8$ from the family of azines and has many excellent physical and chemical properties. It is used for a variety of purposes such as biological staining [13], for medical purposes to investigate viruses [14], as a pH indicator in biochemical systems [15], and in the determination of DNA using optical and electrochemical methods [16]. As a polymer film, PNR has been used as mediator in electrochemical sensors and biosensors [17].

Although there is an extensive literature on the corrosion protection properties of conducting polymers, such as polyaniline and polypyrrole on iron or iron-based alloys [18–20], there are very few reports devoted to copper or copper-based alloys. In the cases where these polymers have been considered, they have first been synthesized chemically, and then deposited at the metal surface, for example by spin coating. Brusic et al. [21] have studied the corrosion protection properties of polyaniline and its derivatives

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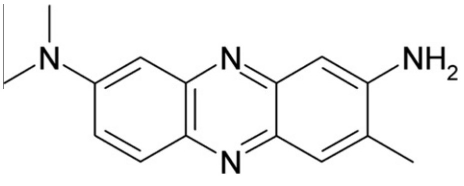

Fig. 1. Chemical structure of neutral red (*N*^{8},*N*^{8},3-trimethylphenazine-2,8,-diamine).

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 lead to significant corrosion protection depending on the chemical nature of the polymer backbone and on the oxidation state and extent and nature of polymer doping. Vera et al. [22] synthesized Pani and Poma (poly(ortho-methoxyaniline)) by chemical oxidation of the monomers and studied the corrosion protection of films obtained on copper (and on carbon steel) and found that the best anti-corrosion efficiency was obtained with Pani due to the formation of an oxide film layer at the polymer–metal interface. These authors also studied the protection of aluminium in galvanic systems using Pani films deposited on copper in copper–aluminium couples used in marine environments [23]. They found that Pani on copper reduces the effective area of copper where oxygen evolution occurs leading to a decrease in the aluminium damage caused by corrosion in the couple.

In this work PNR coatings were produced by in situ electropolymerization on passivated copper substrates by cyclic voltammetry and the corrosion protection of these coatings was studied by open circuit potential measurements, Tafel plots and electrochemical impedance spectroscopy, with morphological examination by scanning electron microscopy.

2. Experimental

2.1. Reagents and solutions

All chemicals were used were analytical reagent grade. The electrolytes used for passivation of copper were 0.125 M sodium oxalate pH 6.85 ($C_2Na_2O_4$, Merck), 0.10 M sodium salicylate pH 6.50 ($C_7H_5NaO_4$, Sigma–Aldrich) and 0.10 M sodium hydrogen carbonate pH 8.35 ($NaHCO_3$, Riedel-de Haën, Germany).

The monomer neutral red (NR) *N*^{8},*N*^{8},3-trimethylphenazine-2,8-diamine was from Aldrich, Germany. A 10 mM NR solution was prepared in 0.025 M potassium phosphate buffer (KPB) pH 5.54 prepared from di-potassium hydrogen phosphate trihydrate ($K_2HPO_4 \cdot 3H_2O$, Panreac, Spain) and potassium dihydrogen phosphate (KH_2PO_4, Riedel-de Haën, Germany).

Corrosion tests were carried out in 0.10 M potassium chloride (KCl, Fluka).

Millipore Milli-Q nanopure water (resistivity > 18 MΩ cm) was used for preparation of all solutions. All experiments were performed at 24 ± 1 °C.

2.2. Electrode preparation

Working electrodes were made from copper cylinders (99.99% purity, Goodfellow Metals, Cambridge, UK) by sheathing in glass and epoxy resin. The exposed disc electrode surface area was 0.20 cm^2. Before experiments, the electrodes were mechanically abraded with 400, 600, 800 and 1500 grade silicon carbide papers. After this procedure, the electrodes were cleaned with water.

2.3. Instrumentation

All experiments were carried out in a three-electrode cell using a modified or unmodified copper working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as reference.

Cyclic voltammetry, open circuit potential and Tafel Plots were done using a potentiostat/galvanostat (Autolab PGSTAT30) connected to a computer with general purpose electrochemical system software (GPES v4.9) from Metrohm-Autolab (Utrecht, Netherlands). OCP was measured on the copper electrodes during 4 h immersion in 0.10 M KCl. Tafel plots were recorded scanning the potential between OCP ± 200 mV with a scan rate of 1 mV s^{-1} after 4 h of electrodes immersion in 0.10 M KCl.

Electrochemical impedance spectroscopy was carried out on a PC-controlled Solartron 1250 frequency response analyzer, coupled to a Solartron 1286 electrochemical interface using ZPlot 2.4 software (Solartron Analytical, UK), with an rms perturbation of 10 mV applied over the frequency range 65.5 kHz–0.01 Hz, with 10 frequency values per decade. The spectra were obtained after 4, 24, 48, 72 and 96 h immersion of the copper or modified copper electrodes in 0.10 M KCl.

Microscope images were acquired on passivated and on PNR-coated passivated copper electrodes using a scanning electron microscope (SEM) Jeol JSM-5310 (Jeol, Tokyo, Japan), equipped with a thermionic field emission SEM and an electronically controlled automatic gun. The images were captured at 20 kV.

2.4. Cu electrode passivation and modification with PNR

Before modification with PNR, the Cu electrodes were first passivated by potential cycling in the ranges -0.5 V(SCE) to +1.0 V(SCE) for sodium oxalate, -1.2 V(SCE) to +1.5 V(SCE) for sodium salicylate and -1.0 V(SCE) to +0.75 V(SCE) for sodium hydrogen carbonate solutions, during 5 cycles at a scan rate of 20 mV s^{-1}.

After passivation, the PNR film was prepared by electropolymerization from an aqueous solution of 10 mM neutral red in 0.025 M KPB pH 5.54 by cycling the applied potential from -1.5 V(SCE) to +1.0 V(SCE) for electrodes passivated in oxalate, -1.2 V(SCE) to +1.5 V(SCE) for electrodes passivated in salicylate or -1.0 V(SCE) to +0.25 V(SCE) for electrodes passivated in hydrogen carbonate, during 15 cycles at a potential sweep rate of 20 mV s^{-1}.

3. Results and discussion

3.1. Passivation of Cu

Before electropolymerization of NR, the Cu electrodes were passivated by potential cycling in oxalate, salicylate or hydrogen carbonate solutions. The deposition of PNR on non-passivated Cu electrodes was not possible, due to very poor adhesion of the film on this surface. The passivation of copper in these media has been previously studied by other authors [4,7–12].

Cyclic voltammograms of Cu electrodes recorded during passivation are shown in Fig. 2. In sodium oxalate solution, Fig. 2a, the formation of an insoluble copper oxalate film on Cu leads to stabilization of the Cu surface [11]. In the first cycle in the positive direction, the dissolution of copper starts at ~ -0.15 V(SCE), indicated by an increase in the current. In the reverse scan, the anodic current remains almost constant until 0.0 V(SCE), indicating that Cu continues dissolving, producing Cu^{2+} ions that interact with the oxalate anions to form insoluble copper oxalate. On further cycling, the anodic peak shifts to more positive potentials, decreasing in height with the number of cycles, suggesting stabilization of the Cu electrode owing to formation of $CuC_2O_4 \cdot H_2O$ on the electrode surface.

The cyclic voltammograms for passivation of copper in salicylate solution, Fig. 2b), exhibit three anodic and three cathodic peaks. The peak at ≈ -0.17 V(SCE) is related to the formation of Cu_2O and that at ~ +0.20 V(SCE) is associated with the oxidation

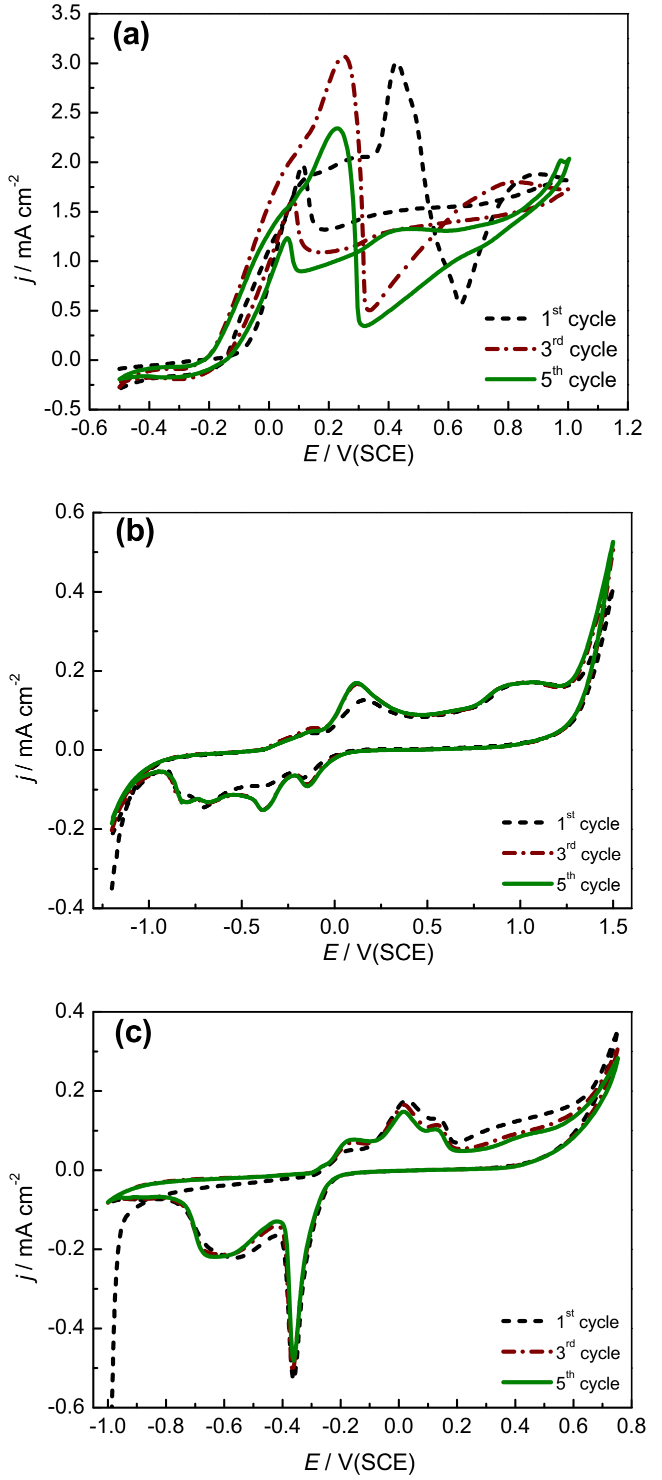

Fig. 2. Cyclic voltammograms of passivation of copper electrodes in sodium (a) oxalate, (b) salicylate and (c) hydrogen carbonate solutions.

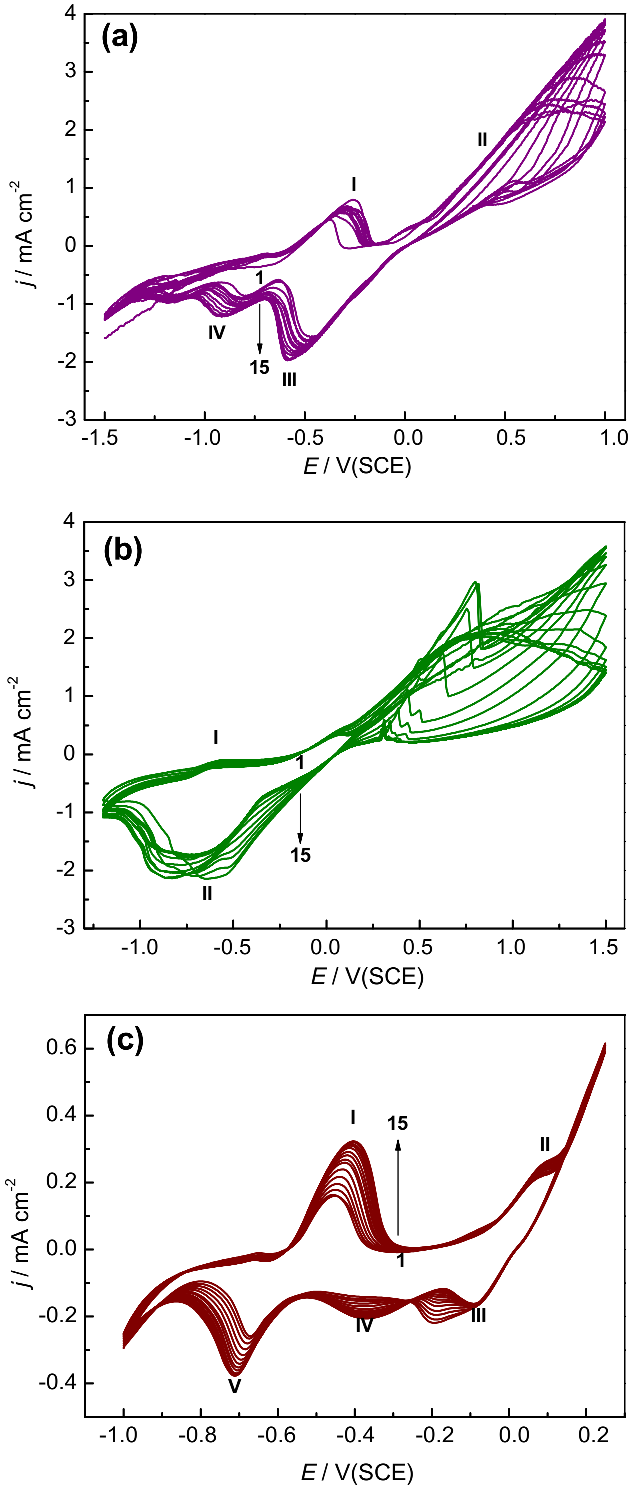

Fig. 3. Cyclic voltammograms of the electropolymerization of neutral red on copper electrodes after passivation in sodium (a) oxalate (b) salicylate and (c) hydrogen carbonate solutions.

of copper and Cu_2O to divalent surface and solution phase species. After this oxidation, a complex of high molecular weight and low solubility is formed between the Cu(II) cations and salicylate anions which precipitates on the metal surface, overlaying an inner Cu_2O layer. This precipitate leads to a diffusion barrier that partially inhibits the dissolution process of copper. The peaks at ~ +0.90 V(SCE) are due to salicylate ion oxidation. The decrease in the anodic current suggests that salicylate anions contribute to the passivation of the copper surface, forming chelates of salicylate and copper ions after adsorption of salicylate anions on metal surfaces [24,25].

Cyclic voltammograms in Fig. 2c in hydrogen carbonate solution show three well-defined anodic peaks observed at ~−0.15 V(SCE), ~0.03 V(SCE) and ~+0.15 V(SCE). Up until the first peak (~−0.15 V(SCE)) during the positive scan Cu(I) dominates so it is expected that the film formed contains just Cu_2O. Above this potential, the dominant species is Cu(II) leading to the formation of a passive film probably of CuO–Cu carbonate. From +0.20 V(SCE) to +0.70 V(SCE) there is an anodic current plateau. Higher values of the potential result in an abrupt increase of the current, indicative of oxygen evolution and of passive film breakdown [9]. Reversing the potential scan shows two cathodic peaks at ∼−0.40 and ∼−0.60 V(SCE) associated with electroreduction of the passive film [26].

3.2. Electropolymerization of neutral red

The formation of a poly(neutral red) film on passivated copper electrodes was carried out by electropolymerization of the neutral red monomer using potential cycling, as described in Section 2. The mechanism of polymerization involves initiation by formation of a cation-radical upon electrooxidation [27].

Fig. 3 shows cyclic voltammograms obtained during the formation of the poly(neutral red) film on the Cu electrodes passivated in oxalate (Fig. 3a), salicylate (Fig. 3b) and hydrogen carbonate (Fig. 3c) solutions.

On copper passivated in oxalate, Fig. 3a, the irreversible monomer oxidation wave at approximately +0.70 V(SCE) shifts with increasing number of cycles to more positive potentials due to electrode surface changes caused by PNR film formation and pH changes at the electrode surface. The anodic current due to oxidation of the monomer to the cation radical (peak II) increases from cycle to cycle similarly to the electropolymerization of pyrrole, aniline and other conducting polymer monomers. The redox pair that appears at negative potentials is due to reduction/oxidation of the polymer film. The redox couple around −0.55 V(SCE) is due to NR-leuco-NR reduction–oxidation and shows polymer growth with an increasing number of cycles. There is rapid polymerization in the 15 cycles employed.

For copper passivated in salicylate, Fig. 3b, there is one cathodic and one anodic peak. The redox couple due to reduction–oxidation of the polymer shows peaks at −0.90 and −0.50 V(SCE) and grows with increasing number of cycles. The reduction peak shifts to more negative potentials with each cycle and, although after seven cycles the reduction peak current starts to decrease, the potential continues to shift to more negative values and the peak becomes broader. This could be related to branching of the PNR polymer chains and changing of the surface structure as well as effects of polymer film resistance and/or diffusion of counterions becoming apparent.

Copper passivated in hydrogen carbonate solution, leads to two anodic peaks and three cathodic peaks, Fig. 3c. The irreversible monomer oxidation wave at approximately +0.10 V(SCE) shifts with the number of scans to more positive potentials due to electrode surface changes caused by PNR film formation and pH changes. The polymer reduction–oxidation couple at −0.70 V(SCE) and −0.40 V(SCE) increases in height with increasing number of cycles. The shift in the reduction peak to more negative potentials again suggests branching of the PNR and counterion diffusion limitations. However, the oxidation peak increases constantly, which confirms the formation of PNR film, in agreement with [27].

3.3. Corrosion studies of PNR-coated passivated copper electrodes

3.3.1. Open circuit potential (OCP)

Open circuit potential measurements were made on bare copper electrodes, after passivation and after PNR coating in 0.10 M KCl electrolyte solution during 4 h of immersion, Fig. 4.

Comparing the OCP profiles obtained for the bare and passivated Cu, different behaviours were obtained with Cu/oxalate and Cu/hydrogen carbonate with OCP values initially more positive than bare Cu, indicating the formation of a passive oxide film layer, and at Cu/salicylate more negative. After 50 min immersion, the Cu/hydrogen carbonate reaches the same value as bare Cu, revealing fracturing of the passivated film.

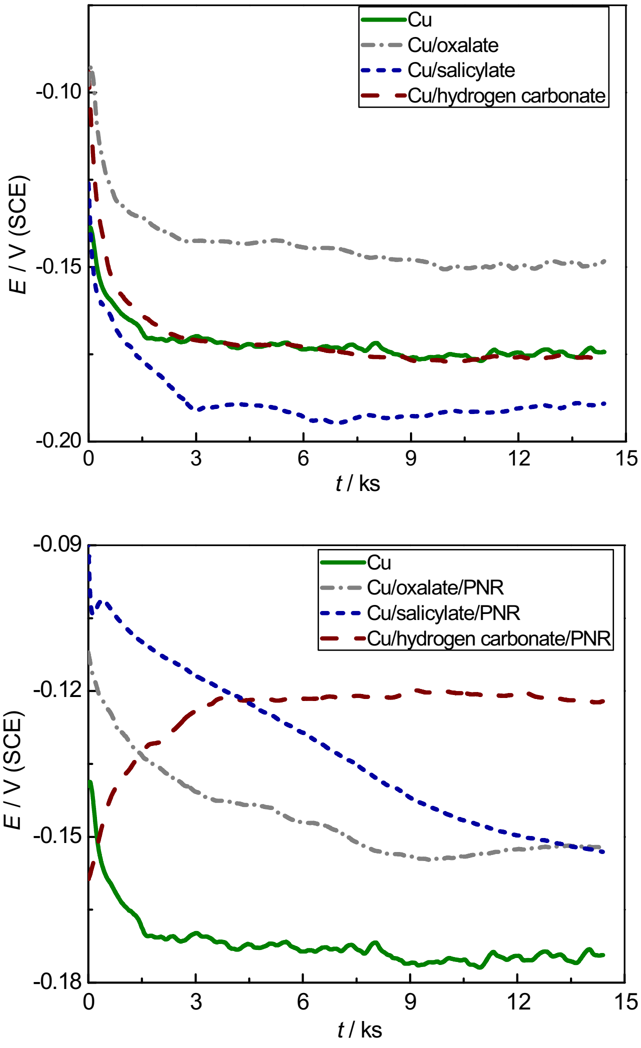

Fig. 4. Open circuit potential variation of the different copper modified electrodes in 0.10 M KCl.

In all cases, after modification of the passivated copper electrode with the PNR films, the OCP is more positive than that of the unmodified bare Cu electrode and of the copper passivated in the different solutions, showing that the PNR films can reduce the corrosion of copper. Regarding the behaviour of Cu/hydrogen carbonate/PNR, the increase in the OCP value can be related to the formation of a passive film formed from species that are thermodynamically more stable than in the other two cases. In the case of the PNR film formed on the Cu electrode passivated in salicylate solution, the OCP value after ∼5 min of immersion in 0.10 M KCl starts to decrease and does not reach a stable value during the 4 h immersion of the modified electrode. This decrease can be attributed to water uptake by the polymer and to diffusion of chloride ions through the PNR film to the copper interface.

3.3.2. Tafel polarization plots

Tafel plots of the bare electrode and with the modifications of the surface after 4 h immersion in 0.10 M KCl solution are shown in Fig. 5 and the parameters calculated from these plots are summarized in Table 1. The anodic and cathodic Tafel coefficients, β_a and β_c, increase after the copper electrode is passivated. Although an increase in β_a will lead to an increase in the corrosion

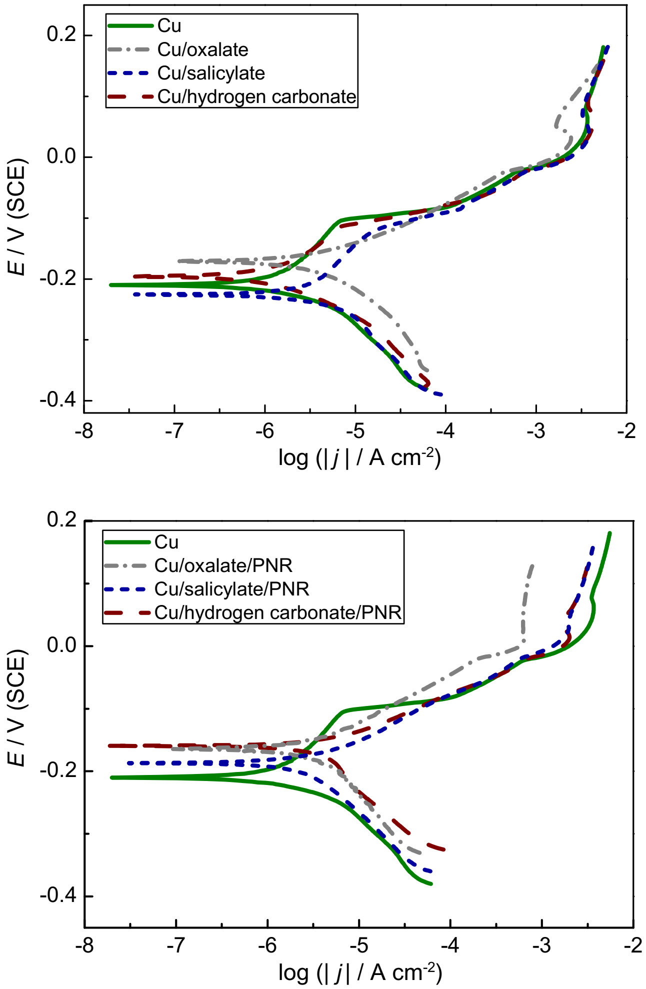

Fig. 5. Tafel plots after 4 h of immersion in 0.10 M KCl.

Table 1
Data from Tafel plots for different modified copper electrodes after 4 h immersion in 0.10 M KCl.

Electrode assembly	R_{ps}/ kΩ cm^2	E_{corr}/ V(SCE)	β_a/ V dec^{-1}	$\lvert\beta_c\rvert$/ V dec^{-1}	P/%	PE/ %
Bare Cu	2.77	−0.221	0.023	0.018		
Cu/oxalate	3.99	−0.167	0.048	0.034	0.31	30
Cu/oxalate/PNR	7.11	−0.163	0.122	0.075	0.12	61
Cu/salicylate	3.42	−0.231	0.030	0.053	30	19
Cu/salicylate/PNR	5.37	−0.186	0.085	0.045	1.6	48
Cu/hydrogen carbonate	4.57	−0.190	0.021	0.024	2.7	39
Cu/hydrogen carbonate/PNR	8.78	−0.160	0.019	0.028	0.07	68

rate, there is also an increase in β_c, showing that anodic dissolution of the metal and the protection conferred by the passivation film is dominated by the cathodic reaction (cathodic protection). In the case of the passivation of copper in hydrogen carbonate solution, β_a decreases slightly and β_c increases, also leading to cathodic protection. This is confirmed by the values of polarization resistance which increase following copper passivation. With the PNR films again β_c increases, and so the cathodic reaction continues to dominate.

Considering that the passive film and the PNR films are electrochemically inert at low anodic overpotential, the porosities of the films were estimated using the following relation [8,28,29]

$$P = \left(\frac{R_{ps}}{R_{pc}}\right) \times 10^{-(|\Delta E_{cor}|/\beta_a)} \qquad (1)$$

where P is the total coating porosity, R_{ps} and R_{pc} are the polarization resistances of the bare copper and the modified copper electrode, ΔE_{cor} is the difference potential between the corrosion potential of modified copper and bare copper electrode, and β_a is the anodic Tafel coefficient for the bare copper. The calculated values are present in Table 1. The porosities decrease after modification of passivated copper with PNR coatings except in the case of oxalate, where the porosity is almost the same as after coating the electrode with PNR. The values of porosity in increasing order were Cu/hydrogen carbonate/PNR < Cu/oxalate/PNR < Cu/salicylate/PNR.

The protection efficiency (PE) can be calculated from the polarization measurements by the expression [8,28,29]:

$$\text{PE\%} = \left(\frac{R_{pc} - R_{ps}}{R_{pc}}\right) \times 100 \qquad (2)$$

where R_{ps} and R_{pc} have the same meaning as in Eq. (1). The values are shown in Table 1. The protection efficiency increases after modification of passivated copper with PNR coatings due to the lower porosity obtained after PNR deposition for the electrodes Cu/hydrogen carbonate and Cu/salicylate. The best efficiency was obtained with PNR deposited on the copper electrode passivated in hydrogen carbonate solution (~68%), followed by PNR in Cu/oxalate electrode (~61%) being less than 50%, i.e. ~48%, for the PNR coating on Cu passivated in salicylate solution.

The values of protection efficiency are in agreement with the calculated film porosities, that are lower for the Cu/hydrogen carbonate/PNR, which has a higher protection efficiency. The morphology of the films varies according to their identity of the film, without and with PNR; however, the surfaces are completely covered. The SEM image in Fig. 6 obtained with Cu/hydrogen carbonate/PNR shows that the passivated copper surface is completely covered by the PNR film, and also shows its low porosity.

Comparison of E_{corr} with the corresponding OCP values shows a small difference in values after the same immersion time, which can be attributed to the effects of polarization, but the order of E_{corr} values is the same, so that the results from the two techniques are in agreement.

3.3.3. Electrochemical impedance spectroscopy measurements

The long-term corrosion behaviour of the PNR coatings on the passivated Cu surfaces was probed by electrochemical impedance spectroscopy. Complex impedance plots obtained at the open circuit potential after 4, 24, 48, 72 and 96 h immersion in 0.10 M KCl are shown in Fig. 7. Analyzing Fig. 7 it can be seen that there

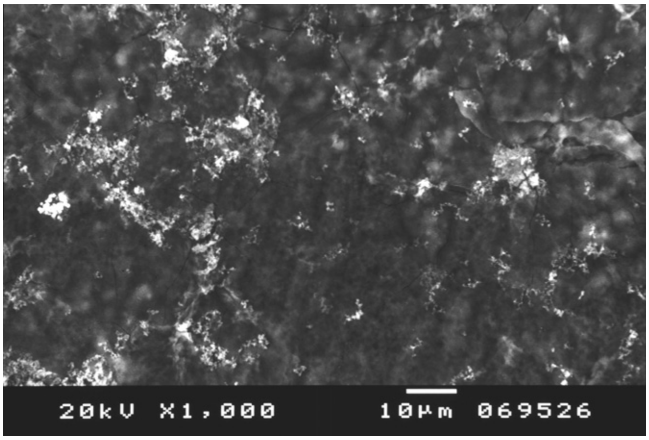

Fig. 6. Scanning electron micrograph of Cu/hydrogen carbonate/PNR surface.

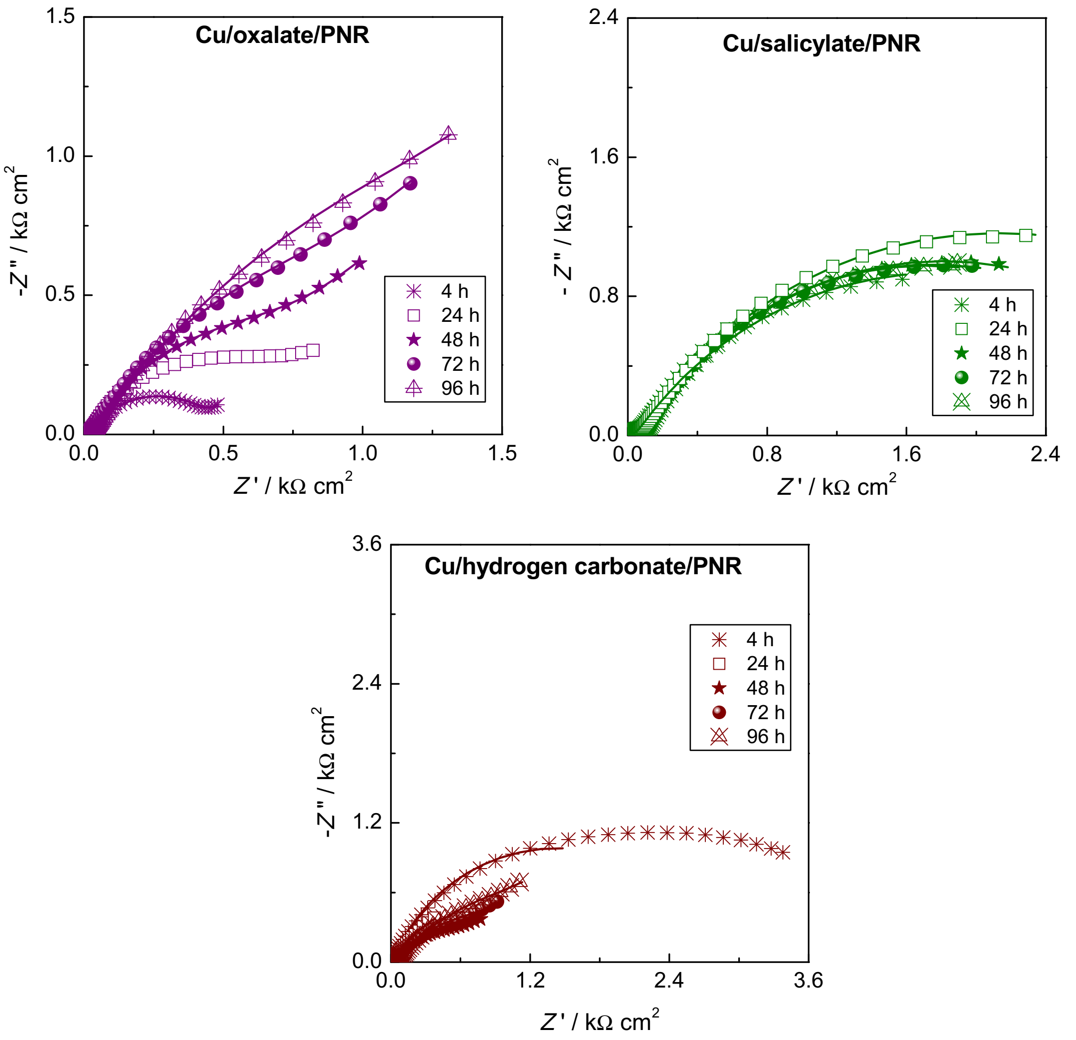

Fig. 7. Complex plane impedance plots of Cu modified electrodes after immersion in 0.10 M KCl. Lines show fitting to the equivalent electrical circuit.

are some differences in the spectra obtained with the polymer-modified electrodes. In the case of the Cu/salicylate/PNR, although there is some decrease in the impedance values after 4 h immersion in 0.10 M KCl, after this time the impedance increases and then becomes almost invariant with time. For the other two types of electrode, at low frequencies the impedance increases with immersion time, being higher for Cu/oxalate/PNR.

The impedance spectra were modelled by the equivalent circuit in Fig. 8 which comprises a cell resistance R_Ω in series with a constant phase element CPE expressed by C_c in parallel with a resistance R_{po}. This resistance is also in series with a *R*CPE combination with R_{ct} the charge transfer resistance in the bottom of the pores of the passivated copper and CPE_2 the non-ideal capacitance of the passivated copper surface inside of the pores, C_2. The characteristics of the PNR film are given by R_{po}, resulting from the formation of ionically paths across the coating, and coating capacitance C_c at high frequencies. At lower frequencies the combination R_{ct} CPE_2 describes the characteristics of the electrolyte/copper interface on the bottom of the pores. This circuit is the same used by other authors to model impedance spectra obtained from polymer-coated metals immersed in corrosive electrolytes [8,28,30–33]. The CPE was found to be necessary due to the heterogeneous nature of the modified copper electrodes. The CPE = $\{(C\,i\omega)^{\alpha}\}^{-1}$ models a non-ideal capacitor of capacitance *C* and roughness factor α, where an α value of 1 represents a perfectly smooth surface.

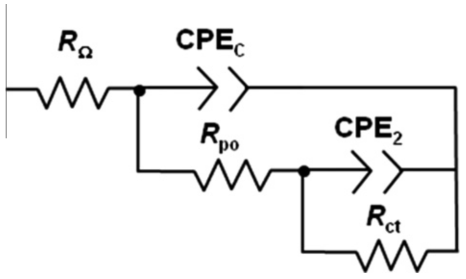

Fig. 8. Equivalent electrical circuit used for modelling impedance spectra in Fig. 7.

Fitting the spectra was attempted with several equivalent circuits in order to clearly justify all the different interfaces of the modified electrodes as well as different physical and electrochemical processes that occurs when the coated electrode is immersed in the corrosive electrolyte solution at different exposure times (electrolyte penetration and/or diffusion in the coating, water uptake, onset of the corrosive processes at the surface of the metal, formation and diffusion of corrosion products and detachment of the coating [28]); however, no good fitting of the experimental data was achieved.

Values of the parameters obtained from fitting are summarized in Table 2. The errors in the fitting of the experimental values to the equivalent circuit varied between 3% and 10% for resistances R_{po} and R_{ct}, 0.8–4% for capacitances C_c and C_2, and less than 1%

Table 2
Data obtained from analysis of the impedance spectra of Fig. 7.

Electrode assembly	Immersion time/h	R_{po}/kΩ cm^2	C_c/μF cm^{-2}	α_1	R_{ct}/kΩ cm^2	C_2/mF cm^{-2}	α_2
Cu	4	1.6	298	0.65	–	2.34	0.88
Cu/oxalate/PNR	4	0.49	345	0.64	1.2	21	0.89
	24	0.92	371	0.68	1.3	7.0	0.84
	48	1.1	379	0.72	2.9	2.2	0.81
	72	2.1	473	0.68	3.8	1.7	0.91
	96	4.4	549	0.63	5.9	2.4	0.93
Cu/salicylate/PNR	4	0.71	234	0.60	3.5	0.23	0.65
	24	0.72	76.1	0.66	4.1	0.21	0.65
	48	0.79	31.6	0.71	3.4	0.26	0.67
	72	0.68	15.1	0.79	3.3	0.31	0.68
	96	0.65	10.6	0.83	3.2	0.35	0.69
Cu/hydrogen carbonate/PNR	4	2.8[a]	47.2[a]	0.77[a]	–	–	–
	24	0.55	1790	0.70	1.5	1.00	0.57
	48	0.91	490	0.65	1.6	4.17	0.77
	72	1.6	582	0.59	2.2	3.84	0.87
	96	2.3	578	0.59	3.0	3.29	0.89

[a] Fitting to "high" frequencies, above 1 Hz.

for α_1 and α_2. The cell resistance increases with immersion time and from 4 to 96 h increases from 15 to 36 Ω cm^2 for the Cu/oxalate/PNR; 23–36 Ω cm^2 for Cu/salicylate/PNR and 15–46 Ω cm^2 for Cu/hydrogen carbonate/PNR.

Except at small immersion times, higher values for R_{po} were obtained with Cu/oxalate/PNR indicating either that the porosity is lower than that of the other modified electrodes or, in the case of higher porosity, the dimensions of the pores are smaller which can make the passage of the ions of the electrolyte through the film difficult. Increasing the immersion time, R_{po} increases for the Cu/oxalate/PNR and Cu/hydrogen carbonate/PNR, presumably due to plugging of defects with corrosion products, covering the pores. Meanwhile, C_c increases for these electrodes with increasing immersion time due to water uptake by the polymer coating. There is also an increase in R_{ct} which can be attributed to an extra anti-corrosive coating formed by the corrosion products at these modified electrodes. After 96 h immersion in 0.10 M KCl, R_{ct} is highest for Cu/oxalate/PNR, which is attributed to a more effective barrier of PNR film on Cu passivated in oxalate solution. Concerning the values obtained with Cu/hydrogen carbonate/PNR after 4 h immersion in 0.10 M KCl, it seems that the PNR film was not stable before the EIS experiment. The time allowed for the film to dry after its electropolymerization from the monomer, seems to be insufficient for its reorganization on the surface of Cu electrode.

A different behaviour was observed with the Cu/salicylate/PNR electrode: R_{po} decreases slightly with increasing immersion time and C_c decreases, with a slight decrease in R_{ct}. From the Tafel plots it was already seen that, at this electrode, the protection efficiency of the PNR coating was less than on the other two electrodes.

The EIS results confirmed that PNR coatings can act as protective films of copper corrosion in 0.10 M KCl, being the best anti-corrosive characteristics obtained in PNR films deposited on copper passivated in oxalate solution.

4. Conclusions

Neutral red has been electropolymerized on copper electrodes by potential cycling. The electrodes were first passivated in different electrolytes: sodium oxalate, salicylate or hydrogen carbonate solutions. This step was necessary due to Cu dissolution at potentials where NR is oxidized. After this, formation of PNR coatings on the Cu surface was performed by potential cycling, within different potential limits depending on the solution where the Cu was passivated.

The behaviour of the modified Cu/PNR electrodes was tested in 0.10 M KCl using OCP measurements, Tafel plots and EIS, leading to the conclusion that PNR improves the corrosion behaviour of copper electrodes.

Although the protection efficiency calculated from Tafel plots after 4 h of immersion in 0.10 M KCl was higher for the PNR coating deposited on Cu passivated in hydrogen carbonate solution (Cu/hydrogen carbonate/PNR), the impedance spectra for longer immersion times showed a better corrosion protection performance with PNR on Cu/oxalate electrodes.

This work shows the versatility of using redox polymers for passivated copper corrosion protection, and opens up the possibility of using phenazine polymers for the anti-corrosion protection of metals.

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