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Protective Effect of Poly(4-Vinylpyridine) Containing Surface Films to the Corrosion of Copper

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Neste trabalho investigou-se a capacidade de filmes de poli(4-vinilpiridina) (P4VP) em melhorar as propriedades de corrosão do cobre em H_2SO_4 0,1 mol L^{-1}. Filmes que formam o complexo macromolecular $Cu(P4VP)_2(SCN)_2$ foram obtidos por métodos eletroquímicos ou espontaneamente (por imersão) em soluções contendo 3% de ácido acético, KSCN 0,1 mol L^{-1} e P4VP. As características morfológicas dos filmes e o seu efeito sobre a corrosão do cobre foram analisados por técnicas de microscopia e eletroquímicas, respectivamente. Um aumento acentuado na resistência à corrosão de amostras de cobre recobertas por filmes de P4VP gerados espontaneamente foi observado em comparação às amostras não recobertas. A melhor condição para a obtenção destes filmes consiste na imersão do cobre em soluções contendo P4VP 0,1 mol L^{-1} durante 3 – 4 h. Empregando-se esta metodologia, registraram-se eficiências de inibição (EI) de 94 – 98%. Para filmes gerados eletroquimicamente, a EI foi de 70 – 85%.

We report here on the ability of poly(4-vinylpyridine) (P4VP) films to improve the copper corrosion properties in 0.1 mol L^{-1} H_2SO_4. Films formed by $Cu(P4VP)_2(SCN)_2$ macromecular-complex were electrochemically or spontaneously (by immersion) grown onto copper surfaces in 3% acetic acid, 0.1 mol L^{-1} KSCN and P4VP containing solutions. Imaging and electrochemical techniques were employed to characterize the film morphology and evaluate its effect on the copper corrosion, respectively. A substantial increase in corrosion resistance of copper samples spontaneously coated by P4VP films was found in comparison to the uncoated ones. The optimum conditions for spontaneous growth comprise a 3 – 4 h immersion period in a 0.1 mol L^{-1} P4VP containing solution. Inhibition efficiencies (IE) of 94 – 98% were recorded by employing this methodology. For electrochemically grown P4VP films, the IE was 70 – 85%.

Keywords: poly(4-vinylpyridine), corrosion, copper

Introduction

The use of d-block metals to produce coordination complexes in polymer blends has been studied over the past few decades.[1] By physically mixing transition-metals cations and coordinating polymers, it has been possible to obtain materials with properties different from those of the individual bulk components.[2,3] Recently, the importance of developing macromolecular complexes was highlighted because of their optical, magnetic, electronic and solution properties.[4] For instance, the conducting and thermal properties of poly(4-vinylpyridine) (P4VP) are significantly changed when the polymer is complexed with copper ions.[5] The technological applications of the P4VP/copper system include reactive blending,[6] catalyst,[7-9] cation exchange resins and membranes designed to preconcentrate metals from dilute solutions[10] or remove them from wastewater,[11] solid-state electrochemical cells,[12] circuit manufacturing on microscopic smoothly polymeric surfaces[13] and anti-corrosion methods.[14]

Poly(4-vinylpyridine)/cupric salts complexes can be synthesized by physical mixing methods, and their thermal and spectroscopic properties are already known.[15] Not surprisingly, exactly the same material can also be obtained by oxidation of a copper electrode or by immersing a copper sheet in P4VP-containing solutions. In these approaches, a green polymer complex is formed on the surface as a film. A straightforward consequence of thereof is that such a film may act as a protective barrier from aggressive media, reducing the dissolution kinetics. To our knowledge, the only

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report on the corrosion of copper in presence of P4VP was given by Abed *et al.*[14] for a Cu60-Zn40 alloy. The authors added P4VP to the working solutions and the corrosion inhibition was controlled by a Frumkin adsorption process.

In this work, we evaluated the protective effect of P4VP containing surface films to the corrosion of copper in sulfuric acid solutions by employing open circuit potential and electrochemical impedance spectroscopy measurements, along with optical and scanning electron microscopy.

Experimental

Synthesis

Working solutions containing 3% acetic acid (Ecibra Reagentes Analíticos), 0.1 mol L^{-1} potassium thiocyanate (Merck) and 0.1 mol L^{-1} (in terms of monomeric units) P4VP (Scientific Polymer Products, linear, MW 200000 g mol^{-1}) were employed in this study. P4VP containing surface films were obtained by two different approaches.

Electrochemical experiments were carried out employing a Voltalab PGZ100 Radiometer Copenhagen potentiostat interfaced to a computer running the VoltaMaster 4.0 software for data acquisition and analysis. A conventional three-electrode cell with a graphite rod as counter electrode and saturated calomel reference electrode (SCE) connected to the cell by a bridge and a Luggin-Habber capillary. All potentials in the text are quoted to this electrode. The working electrode was a 0.52 cm^2 copper plate (99.99%) mounted in a glass tube with Araldite® epoxy. Prior to the experiments, the electrode surface was polished with emery paper, followed by 1.0 and 0.05 μm alumina. Subsequently the electrode was cleaned ultrasonically, degreased with acetone, rinsed with deionized water and air-dried. Experiments were run using cyclic voltammetry between the cathodic (-1.05 V) and anodic (+1.00 V) switching potential limits ($E_{\lambda,c}$ and $E_{\lambda,a}$, respectively). The scan rate varied from 8 to 100 mV s^{-1}. The influence of the number of cycles and P4VP concentration were also investigated.

The spontaneous film growth was studied through immersion of 1.0 cm^2 copper plates of known mass prepared as above described in 0.005 – 0.100 mol L^{-1} P4VP-containing solutions during different periods ranging from 2 to 72 h. Before measuring the mass gain due to the P4VP containing film, the specimens were removed from the solution, rinsed with water and dried at room temperature.

Evaluation of the protective effect

In order to verify the protective effect of the film to the corrosion of copper, the electrode was removed from the working P4VP-containing solution where cyclic voltammetric experiments were performed between $E_{\lambda,c}$ and $E_{\lambda,a}$, rinsed with deionized water and immediately transferred to an electrochemical cell filled with a 0.1 mol L^{-1} H_2SO_4. Then, the open circuit potential (OCP) was measured during 1.0 h. At the OCP recorded after 1.0 h, the electrochemical impedance spectroscopy experiments were carried out in the frequency range 50 kHz - 5 mHz using a 10 mV amplitude sine wave in the same apparatus. For surface analysis, a Neophot 30 optical microscope and a Philips XL-30 scanning electron microscope were employed. The surface chemical composition after the corrosion tests was determined by an Energy Dispersive Spectroscopy (EDS) apparatus coupled to the Philips XL-30 microscope.

Results and Discussion

Electrochemical approach

Figure 1 shows successive cyclic voltammograms recorded at scan rate (v) of 100 mV s^{-1} in a solution containing 0.1 mol L^{-1} P4VP, 0.10 mol L^{-1} KSCN and 3% acetic acid (added to dissolve the polymer). In the first positive going scan, an oxidation process relative to Cu(0)/Cu(I) reaction appears at around -0.45 V (peak I). The Cu(I) ion generated at the electrode/solution interface induces a complexing reaction with P4VP and SCN^-, yielding a polymer complex as product, whose metallic center is further oxidized to Cu(II) in the subsequent electrochemical process (peak II). After the first cycle, the voltammetric profile was considerably distinct exhibiting a decreased in current density relative to Cu(0)/Cu(I) reaction, whereas current associated to the Cu(I)/Cu(II) oxidation remained slowly increasing as function of the

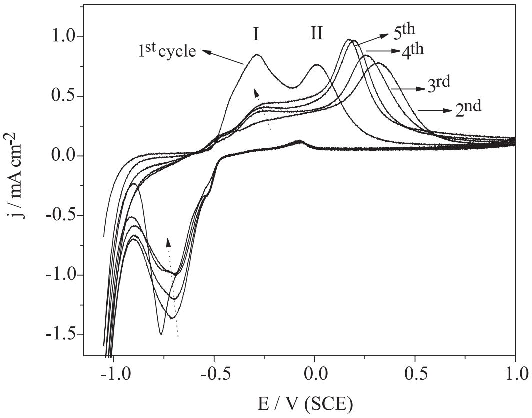

Figure 1. Successive cyclic voltammograms of a copper stationary electrode immersed in an aqueous solution containing 3% acetic acid, 0.10 mol L^{-1} both KSCN and P4VP at v = 100 mV s^{-1}.

number of cycles up to five cycles. Upon successive cycling, the resulting polymer complex grows onto the electrode surface as a slightly adherent green film. This film was found to present the same composition and spectroscopic properties as those observed for polymer complexes synthesized by mixing each component in the proportion of 2:1:2 P4VP:Cu(II):SCN in a common solvent.[15,16] The material presented a Cu(II) metallic center surrounded by nitrogen pyridinic rings and thiocyanide ions (Figure 2).[15] Although there exist a certain degree of reversibility regarding the redox processes in Figure 1, Cu(II) must be the predominant oxidation state in the resulting green film, independently of the ending potential. The fact that the film was green-colored suggests that Cu(II) was the predominant oxidation state, provided that a Cu(I)-film would be colorless since no d-d electronic transitions are feasible to take place in a d^{10} system, and metal-to-ligand charge transfer possible for a d^{10} complex with aromatic structures also does not occur in the visible region of the spectrum.

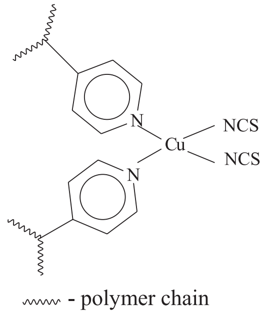

Figure 2. Schematic chemical structure of the $Cu(P4VP)_2(SCN)_2$ complex.

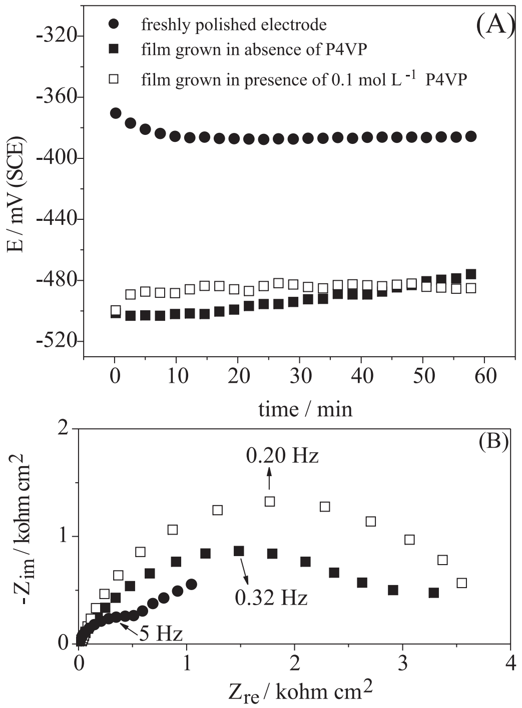

Figure 3. OCP curves (A) and Nyquist diagrams (B) of a copper stationary electrode immersed in 0.1 mol L^{-1} H_2SO_4 after five cycles between -1.05 and 1.00 V at v = 16 mV s^{-1} in presence of 0.1 mol L^{-1} P4VP in the preceding film growth step.

Figure 3 shows the open circuit potential (OCP) curves (A) and the Nyquist diagrams recorded for copper electrodes immersed in 0.1 mol L^{-1} H_2SO_4 without any protective film or with films electrochemically grown by cyclic voltammetry at scan rate of 16 mV s^{-1} in absence and in presence of P4VP. After 60 min of exposure, the uncoated electrode exhibited an OCP of -380 mV. For copper stationary electrodes submitted to five cycles between -1.05 and +1.00 V, the OCP after 60 min of immersion was close to -480 mV regardless of the presence of P4VP during the preceding experimental step. The P4VP effect on the corrosion of copper was, however, pointed out in the Nyquist diagrams shown in Figure 3B. From the Nyquist diagram of a freshly polished electrode, one capacitive loop at the higher frequency range followed by the Warburg impedance at lower frequency values was perceived, in agreement with Villamil *et al.*[17] On the other hand, basically one depressed semicircle was observed for electrodes submitted to cycling. Here, our interest was focused on the charge transfer resistance (R_{ct}) variation depending on the experimental conditions in which the film was obtained. R_{ct} was calculated from the difference in impedance at lower and high frequencies by employing a non-linear least squares fitting, as previously reported and discussed.[18,19] The inhibition efficiency (IE) was calculated according to equation 1:[20]

$$IE\ (\%) = [(R^{-1}_{ct(absence)} - R^{-1}_{ct(presence)}) / R^{-1}_{ct(absence)}] \times 100 \quad (1)$$

where $R_{ct(absence)}$ and $R_{ct(presence)}$ are the charge transfer resistance measured in 0.1 mol L^{-1} H_2SO_4 for freshly polished copper electrodes and containing a film, respectively. The IE was 81% for electrodes coated by the $Cu(P4VP)_2(SCN)_2$ polymeric complex (R_{ct} = 3.82 kohm cm^2), and 76% for electrodes submitted to cycling in absence of P4VP (R_{ct} = 2.99 kohm cm^2). The charge transfer resistance of the freshly polished electrode was 0.72 kohm cm^2.

Figure 4 shows the OCP curves (A) and the respective Nyquist diagrams (B) for a copper stationary electrode immersed in 0.1 mol L^{-1} H_2SO_4 after five cycles between -1.05 and 1.00 V at different scan rates (v) in the film growth step in presence of 0.1 mol L^{-1} P4VP. It is observed that for copper electrodes coated with P4VP films (here and throughout the text $Cu(P4VP)_2(SCN)_2$ film are addressed

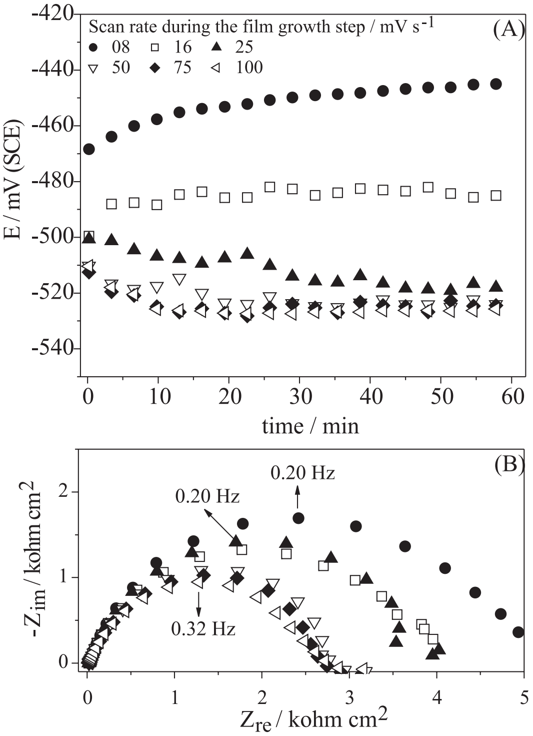

Figure 4. OCP curves (A) and Nyquist diagrams (B) of a copper stationary electrode immersed in 0.1 mol L^{-1} H_2SO_4 after five cycles between -1.05 and 1.00 V at different scan rates (v) in presence of 0.1 mol L^{-1} P4VP in the preceding film growth step.

as P4VP films) obtained at slow scan rates (8 and 16 mV s^{-1}) the OCP recorded after 60 min of immersion shifted towards positive values (Figure 4A). In the Nyquist diagrams shown in Figure 4B, the R_{ct} was higher for slow scan rates; for v = 8 mV s^{-1} the R_{ct} was 4.77 kohm cm^2 whereas for v = 50 mV s^{-1} it decreased to 2.76 kohm cm^2. For v > 50 mV s^{-1}, R_{ct} was almost constant, the values ranging from 2.40 to 2.70 kohm cm^2. The inhibition efficiency calculated according to eq. 1 using the R_{ct} values from the Nyquist diagrams shown in Figure 4B and those obtained for electrodes submitted to cyclic voltammetry at different v in absence of P4VP (data not shown) was in the range of 70 – 85%.

The effect of the number of cycles (*nc*) and P4VP concentration on the copper corrosion resistance were also studied (data not shown). To investigate the influence of *nc* both the P4VP concentration and the scan rate during the film growth step were kept at 0.1 mol L^{-1} and 16 mV s^{-1}, respectively. A well-defined behaviour was found regarding the OCP curves. OCP recorded after 60 min of immersion in 0.1 mol L^{-1} H_2SO_4 changed towards more positive values as the number of cycles increased. For *nc* = 1 the OCP was -550 mV while for *nc* = 10 it was -500 mV. The displacement of OCP to more positive values is related to the structural arrangement,[21] which certainly differ upon varying the number of cycles. The same remarks can be applied with respect to the R_{ct} values obtained from the Nyquist diagrams. The IE was in the range of 65 – 82%.

The influence of the P4VP concentration during the film growth step was also studied. P4VP concentrations ranging from 0.005 to 0.100 mol L^{-1} were investigated keeping the number of cycles and scan rate constant at 5 cycles and 16 mV s^{-1}, respectively. The OCP curves registered in 0.1 mol L^{-1} H_2SO_4 for P4VP coated electrodes showed a behavior similar to that above shown in Figure 3A for 0.1 mol L^{-1} P4VP. The OCP observed after 60 min of immersion was practically constant, ranging between -485 and -475 mV for all the concentrations studied. On the other hand, the R_{ct} extracted from the impedance diagrams presented a nearly linear dependence on the P4VP concentration. For copper electrodes coated in 0.005 mol L^{-1} P4VP solutions, the R_{ct} was 1.97 kohm cm^2 while for those coated in 0.1 mol L^{-1} P4VP solutions R_{ct} was 3.82 kohm cm^2. Furthermore, R_{ct} values higher than 2.99 kohm cm^2 (in absence of P4VP – Figure 3B) were only obtained when P4VP content was higher than 0.01 mol L^{-1}.

Spontaneously coated copper surfaces

While we had been carrying out the electrochemical experiments we observed that these films could also be obtained by immersion, depending on the experimental conditions. Indeed, films exhibiting better ability to improve the corrosion resistance of copper in sulphuric acid medium have been obtained by employing this simplified strategy, as shown in the following paragraphs.

Figure 5 shows the mass gain (in mg cm^{-2}) as function of the immersion time for copper coupons immersed in solutions with different P4VP contents. A mass gain was observed for practically all the samples. For 0.010, 0.050 and 0.100 mol L^{-1} P4VP, however, the mass gain was more pronounced. This process was followed by imaging techniques and electrochemical impedance measurements.

Figure 6 shows optical images of copper coupons immersed during 4 h in P4VP containing solutions. Figure 6A shows the surface morphology of a sample before immersion for the sake of comparison, where the irregularities due to the mechanical treatment are evident. In Figure 6B the surface condition of a sample immersed in a P4VP free solution, *i.e.*, 0.1 mol L^{-1} KSCN and 3% acetic acid solution, is shown. The darkness in this image in comparison to the others is due to a CuSCN layer formed in presence of thiocyanide ions through a dissolution-precipitation reaction yielding a black insoluble cuprous salt as product. In Figures 6C – 6F it is possible to observe the P4VP concentration effect on the spontaneous $Cu(P4VP)_2(SCN)_2$ film growth. **a** and **b** indicate coated and uncoated regions, respectively. However, the presence of a non-homogeneous film, principally in Figures 6C – 6D, is not related to spontaneous growth itself, but a result of the handling procedures. By removing the specimens from the solution, the films become dried as solvent evaporates, and afterwards the coats become easily detachable. This fact can be avoided by maintaining the coupons in water or even directly transferring them to the sulphuric acid solution for corrosion evaluation. Despite this, films grown by immersing the copper specimens in 0.1 mol L^{-1} P4VP were not apparently susceptible to this problem (Figure 6F), comprising, as consequence, the best condition for corrosion purposes.

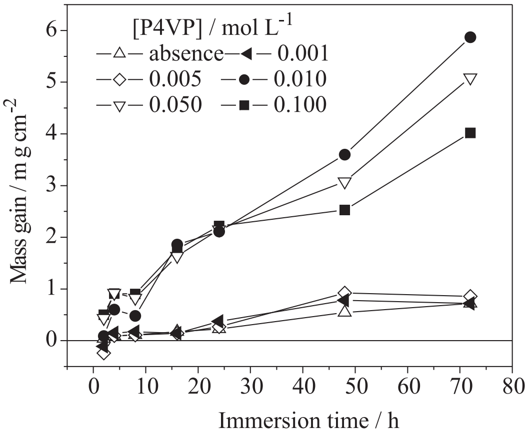

Figure 5. Mass gain as function of the immersion time for copper coupons immersed into solutions with different P4VP concentrations.

Figure 7 shows optical micrographs of copper samples immersed during different periods in a solution containing 0.1 mol L^{-1} P4VP. The micrograph of a specimen before immersion is given in Figure 7A for comparison. An immersion time of 4 h (Figure 7B) clearly gave the best results in terms of homogeneity of the film, so that the ideal immersion time is 3 – 4 h.

Scanning Electron Microscopy (SEM) was employed to obtain micrographs of samples immersed in P4VP free and 0.1 mol L^{-1} P4VP solutions during 4 h (Figure 8). Figures 8A shows the film morphology of a specific case where the film dropped. By comparing Figure 8A with 8D (a sample immersed in a P4VP free solution), a remarkable

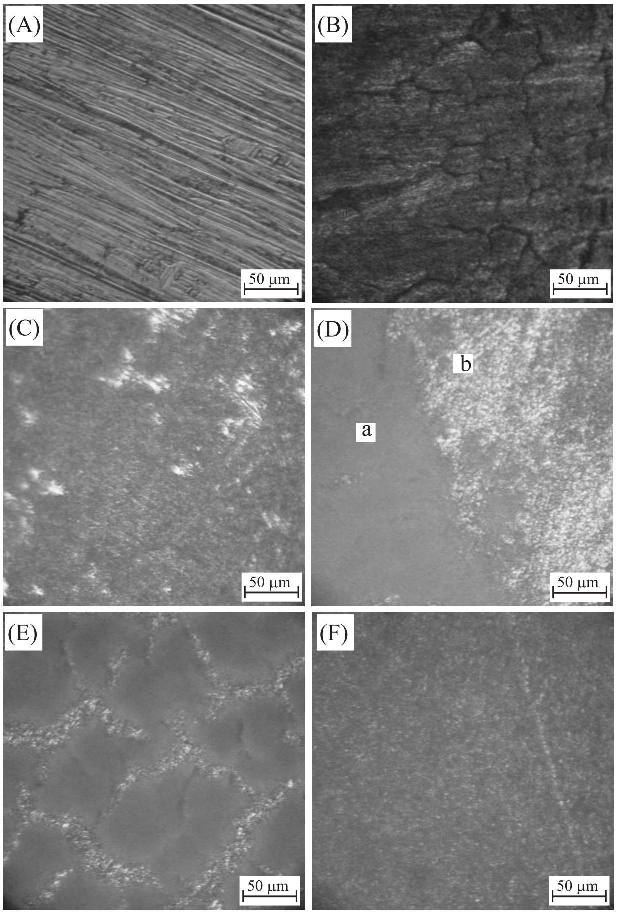

Figure 6. Optical images of copper coupons immersed for a 4 h period in solutions containing distinct P4VP contents (in mol L^{-1}): A) before immersion; B) in absence of P4VP; C) 0.005; D) 0.010; E) 0.050; F) 0.100.

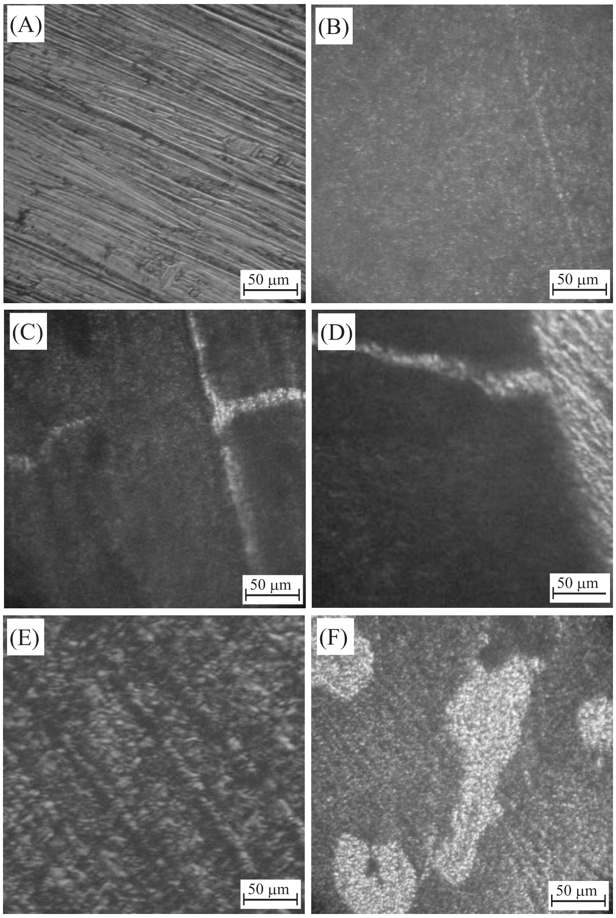

Figure 7. Optical images of copper coupons immersed in a 0.1 mol L^{-1} P4VP containing solution during different periods (in hours): A) 4 (before immersion); B) 4; C) 8; D) 16; E) 24; F) 72.

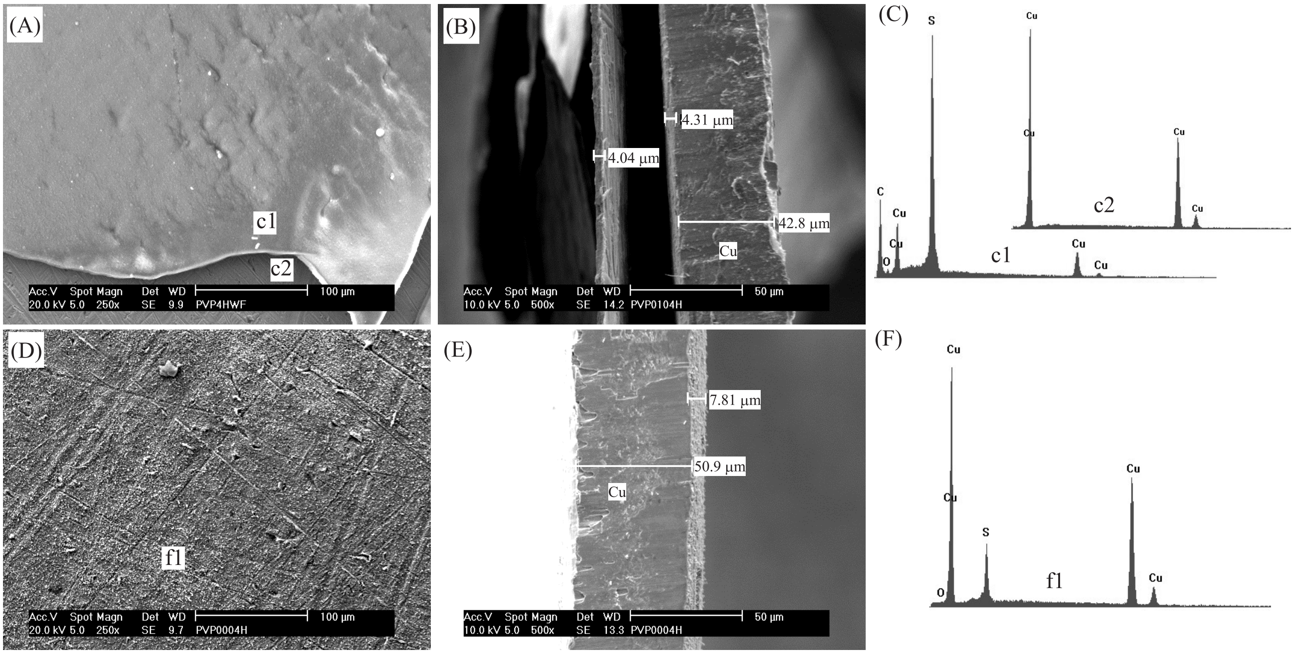

Figure 8. SEM micrographs and EDS spectra of samples immersed in 0.1 mol L^{-1} P4VP containing (A – C) and P4VP free solutions (D – F) during 4 h. The micrographs B and E depict a cross-sectional view of A and D, respectively. c1, c2 and f1 illustrate regions where the EDS spectra were taken.

difference in the surface is noticed, the latter being more irregular. This difference may be interpreted in the light of the film growth mechanism. Presumably, as the complexing reaction goes on, the surface gets smoothed because copper "dissolves" to generate the macromolecular complex. An additional indicative of this effect is shown in Figures 8B and 8E. Figure 8B shows a cross-sectional view of a copper sheet. In this figure, two layers can be clearly observed. The outer one (4.04 μm), which is standing apart in Figure 8B, corresponds to the $Cu(P4VP)_2(SCN)_2$ film, whereas the inner layer (4.31 mm) comprises copper oxides (there is no sulphur related EDS signals in this layer as shown in Figure 8C (spectrum c2)). Specimens immersed during 4 h in P4VP free solutions presented a 7 – 8 μm covering layer whose composition present CuSCN (see the sulphur related EDS signal in Figure 8F, spectrum f1) in addition to oxides. Therefore, in presence of P4VP, the spontaneously formed layer reduces the thickness and changes the composition of the inner layer.

In order to verify the ability of spontaneously grown P4VP films to improve the corrosion resistance of copper, open circuit potential and electrochemical impedance measurements were performed during the growth step and in 0.1 mol L^{-1} H_2SO_4 (Figure 9). Figure 9A shows the OCP variation of a copper electrode immersed in a 0.1 mol L^{-1} P4VP solution during 14 h. Following the immersion, an OCP displacement towards negative values occurred up to 30 min. Subsequently, it started to increase, so that after 5 – 6 h of immersion a new decrease took place, followed by a slowly increase onwards. Surprisingly, the maximum in the OCP curve, which is observed around 4 – 6 h in Figure 9A, seems to coincide with the ideal immersion time discussed above on basis of optical imaging results. At the best of our knowledge, an explanation to this remark remains unclear.

Figure 9B represents the Nyquist diagrams for copper electrodes in P4VP containing solutions recorded at OCP conditions after different periods of immersion, as indicated by arrows in Figure 9A. In general, an increase in the impedance arcs was observed as time increased, reflecting the film growth process. The same electrode was, in the sequence, removed from the P4VP containing solution and immediately transferred to a 0.1 mol L^{-1} H_2SO_4 solution (avoiding drying), in which the EIS measurements shown in Figure 9C were performed. In Figure 9C, a noteworthy augmentation in the resistance at lower frequencies was observed for electrodes exposed to 0.1 mol L^{-1} P4VP containing solutions during 14 h in comparison to electrodes exposed to P4VP free solutions during the same period, indicating clearly a substantial improvement in the corrosion resistance. The impedance response in Figure 9C showed a highly depressed semi-circle, in contrast to Figure 4B where one capacitive loop close to semi-circle was observed. Therefore, the inhibition efficiency (IE), which was 97% and taken according to eq. 1 as for Figure 4B, must be cautiously considered in the present case,

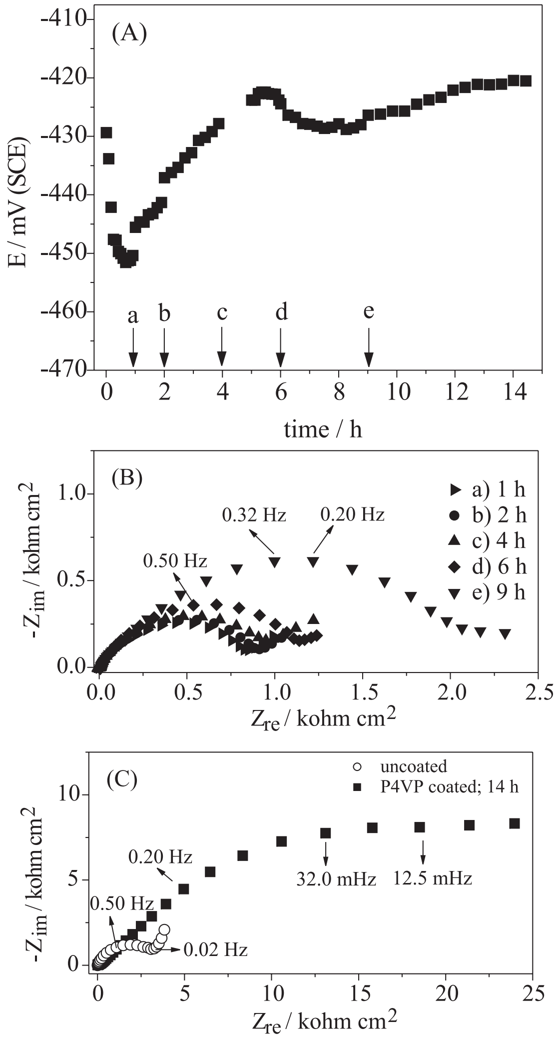

Figure 9. OCP curves (A) and Nyquist diagrams (B) recorded during the spontaneous growth process of a P4VP film in a 0.1 mol L^{-1} P4VP. The arrows indicated periods at which the impedance measurements were performed. After 14 h, the sample was transferred to a 0.1 mol L^{-1} H_2SO_4 solution and the Nyquist diagrams shown in (C) were obtained.

even though the charge transfer resistance was obviously higher for coated electrodes than for uncoated. The same comments can be also extended to any sample coated by immersion for at least 3 hours, the IE ranging between 94 – 98%. However, the resistance decreased gradually as the film became more penetrated by the aggressive solution. After around four hours exposure in 0.1 mol L^{-1} H_2SO_4, the IE attained a constant value close to that recorded for electrodes submitted to cycling in P4VP free solution. Therefore, the chemical stability of these P4VP containing surface films lasted up to 4 h in 0.1 mol L^{-1} H_2SO_4.

Conclusion

In this work, the anti-corrosion properties of P4VP films grown onto copper surfaces were exploited. The complex $Cu(P4VP)_2(SCN)_2$ was obtained by both electrochemical and immersion methods. The electrochemical impedance results together with imaging techniques demonstrated a remarkable improvement of the corrosion resistance of copper in sulphuric acid for specimens spontaneously coated by immersion into a P4VP containing solution. The best condition to obtain such films is by immersing a sample in 0.1 mol L^{-1} P4VP containing solution for a 3 – 4 h period. Afterwards, the covered sample should be transferred to the aggressive media. Inhibition efficiencies (IE) in the order of 94 – 98% are obtained by this methodology. For electrochemically P4VP coated electrodes, the IE ranged between 70 – 85%.

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