X-Ray Photoelectron Spectroscopy Study of the Composition of Polyphenol Films Formed on Pt by Electropolymerisation of Phenol in the Presence of Sulphide in Carbonate Medium

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ABSTRACT: The chemical composition and structure of polyphenol films formed electrochemically on Pt from bulk phenol in the absence and in the presence of solution sulphide were studied by XPS. The C1s (284.2–284.6 and 285.6–286 eV) and the O1s (533 eV) signals are consistent with a polymeric structure consisting of an aromatic carbon ring backbone linked by ether-like bonds and with hydroxyl groups. This structure is common to all the examined films formed under either potentiodynamic or potentiostatic conditions, even though the coatings formed in the presence of sulphide seemed to possess a higher ether-like oxygen content. Polyphenol films generated by cyclic voltammetry in the presence of sulphide contained a small amount of incorporated sulphur, with a characteristic binding energy of 162.3 eV which is essentially identical to that found for a sulphur layer deposited on Pt from sulphide in phenol-free solutions. The film is described as a S-polyphenol composite material, in which the S fraction is mainly incorporated at the early stages of filming. Sulphur-polyphenol composite coatings proved to possess more effective barrier properties than S-free polyphenol films.

KEY WORDS Cyclic Voltammetry / X-Ray Photoelectron Spectroscopy / Sulphur / PPO / Corrosion Inhibition / Barrier Film /

Protective coatings made of certain conducting or insulating polymeric films (or a blend of both) have proved to be effective against metallic corrosion.^{1–6} Conducting polymeric films can impart active protection by exchanging electrons with the metallic substrate, generally pushing the corrosion potential into the passive region. This fact is not, however, sufficient for a successful protection. Tight adherence to the surface, high mechanical strength, film integrity and insolubility are mandatory requisites. Many insulating polymers meet these requirements and, provided they behave as strong physical barriers against corrosive electrolyte penetration, can effect satisfactory protection degrees. Despite their non-electroactive nature, thin insulating films can be formed onto metallic or semiconducting substrates by electropolymerisation from the bulk monomer, before dielectric properties manifest and the film growth is inhibited. Thus, the coating process can also benefit from the advantages of electrochemical methods, namely, simplicity, and flexibility of the experimental apparatus, efficient coating of not readily accessible areas and higher homogeneity of the films.

Among insulating polymers, polyphenol films (also called polyoxyphenylene, poly(phenylene) oxide or PPO films) have received much attention.^{1, 2, 7–20} These films were electropolymerised from phenol or phenol derivatives in a wide variety of electrolytic media, ranging from organic^{9, 17} to hydroalcoholic^{1, 2, 7, 10} to aqueous solutions^{8, 12–16, 18–20} at various pH. The role of several ring substituents was checked in order to increase the monomer solubility in the working electrolyte, to direct the oxidative coupling mechanism to desired ring positions^{1, 8, 9, 13, 16} or to condition the film permselectivity.^{15, 17} Electrogenenerated polyphenol coatings were found to impart promising corrosion protection to steel anodes in contact with various artificial aggressive solutions^{1, 2, 10, 19} or filtering solutions from calcium aluminate cement and Portland cement slurries.²⁰

Much effort has also been devoted to the investigation of phenol electropolymerisation in the presence of additives, whenever the formation of insoluble, thicker films with enhanced barrier properties (strongly reticulated or cross-linked structures) or preservation of metal dissolution during polymerisation (if conducted

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on active metals) were sought. Some successfully tested additives included aliphatic amines^{2, 7, 11} and ammonia compounds,¹⁰ especially ammonium sulphide. The beneficial action of this latter compound was attributed mainly to the inhibition of surface passivation by ammonium, while the role of sulphide remained unclear, although the presence of S within the coating was confirmed.

In a previous paper,¹⁸ the influence of sulphide on the properties of polyphenol films electropolymerised on a model inert substrate such as Pt was examined in carbonate aqueous solutions. Films generated in the presence of sulphide showed enhanced barrier properties and lower permeability to water and to the model ferrocyanide/ferricyanide redox couple. Best results were found for sulphide concentrations in the 10^{-4} M range. The FTIR-ATR inspection of the films evidenced the preservation of the aromatic ring structure and ether-like links between benzene rings. However, no specific structural or compositional differences with respect to polyphenol coatings obtained from sulphide-free solutions could be detected. Moreover, the incorporation of S atoms within the film could not be corroborated by Fourier Transform-Infrared (FT-IR) spectroscopy or EDAX measurements.

In this work, we address the characterisation of polyphenol films formed on Pt in the presence of sulphide by means of X-Ray photoelectron spectroscopy (XPS). The high surface sensitivity of this probe allowed us to ascertain whether or not sulphur-containing species are present within the coating and shed some light on its chemical composition. Results were expected to help clarifying the role of sulphide ions in the exacerbation of the barrier properties of polyphenol films. Also, the far superior barrier properties of polymeric films deposited potentiodynamically over those formed potentiostatically will be correlated with different elemental composition.

EXPERIMENTAL

All reagents employed in this work were of analytical grade (Merck). Test (0.1 M Na_2CO_3) and working solutions (6×10^{-2} M phenol, 10^{-4} M Na_2S , and 6×10^{-2} M phenol + 10^{-4} M Na_2S in 0.1 M Na_2CO_3) were prepared by using ultrapure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) from a Millipore Milli-Q system. These solutions were de-aerated prior to electrochemical measurements by bubbling N_2 . The solutions were blanketed with a stream of N_2 during all electrochemical experiments.

Cyclic voltammetry and potentiostatic polarisation experiments were carried out in an all-Pyrex glass cell with provision for a standard three-electrode assembly.

Cyclic voltammograms were recorded at room temperature and at a sweep rate of 50 mVs^{-1} . The working electrodes (99.99% purity) were bead-shaped Pt for purely electrochemical experiments and Pt disks (8 mm in diameter) for XPS analysis. A Pt coil was used as the counter-electrode. All potentials are referred to a reversible hydrogen electrode (RHE) in contact with the test or working solutions.

Prior to each electrochemical experiment, Pt electrodes were flame-cleaned, quenched in ultrapure water and brought into contact with the working solution. After the desired film was formed on the surface, Pt samples were emersed at the selected potential, withdrawn from the working cell, thoroughly rinsed with ultrapure water and transferred to either a secondary electrochemical cell with 0.1 M Na_2CO_3 solution for the voltammetric characterisation of the film or to the ultrahigh vacuum (UHV) analysis chamber for XPS measurements. Emersed Pt specimens for surface analysis were first dried under a stream of pure N_2 .

XPS analysis was conducted at a base pressure of 5×10^{-10} mbars and a temperature at around 173 K . The XPS spectra were obtained with a VG-Microtech Multilab electron spectrometer by using unmonochromatized $\text{MgK}\alpha$ (1253.6 eV) radiation from a twin anode source operated at 300 W (20 mA , 15 kV). Photoelectrons were collected at a take-off angle of 90° into a hemispherical analyser working in the constant energy mode at a pass energy of 50 eV . Spectral resolution ranged from 0.10 to 0.15 eV . The binding energy (BE) scale was calibrated with reference to the $\text{Pt}4f_{7/2}$ line at 71.0 eV . Charging corrections seemed not necessary. Peak BEs were given with an accuracy of $\pm 0.2 \text{ eV}$. Curve fitting was done with mixed Gaussian/Lorentzian function lineshapes by using the Peak-fit program implemented in the control software of the spectrometer. Core-level S2p photoemission transitions were deconvoluted by locking the $2p_{3/2}:2p_{1/2}$ intensity ratio to the theoretical value 2:1 and the spin-orbit splitting to $1.1\text{--}1.2 \text{ eV}$. The full width at half maximum (FWHM) was close to $1.9\text{--}2.0 \text{ eV}$. Peak areas were corrected with proper sensitivity factors stored in the software package database.

RESULTS AND DISCUSSION

Electrochemical Generation of Polyphenol Films

The voltammetric curves corresponding to the first cycle of a 25-scan electropolymerisation programme imposed to a Pt electrode in a 0.1 M Na_2CO_3 solution containing 6×10^{-2} M phenol (solid line) and 6×10^{-2} M phenol + 10^{-4} M Na_2S (dashed line) are depicted together in Figure 1. In the absence of solu-

Figure 1. First cyclic voltammogram for a Pt electrode in: a 6×10^{-2} M phenol + 0.1 M Na_2CO_3 solution (solid line); 6×10^{-2} M phenol + 10^{-4} M Na_2S + 0.1 M Na_2CO_3 solution (dashed line).

tion sulphide, the oxidation of phenol starts up at about 0.75 V and shows a sharp and irreversible peak at nearly 1.25 V, which is followed by partial surface oxide formation. When sodium sulphide is added to the working solution, the anodic current appears at a potential as low as 0.3 V and rises to delineate a weaker oxidation peak. In both cases, successive scanning between 0.06 and 1.5 V (not shown) leads to the progressive deactivation of the Pt surface originated by the formation of an insulating polyphenol film.¹⁸

In an early work,¹⁸ it was stated that the characteristic redox peaks for the model $[\text{Fe}(\text{CN})_6]^{-3}/[\text{Fe}(\text{CN})_6]^{-4}$ couple are fully precluded by polyphenol coatings built in either the absence or the presence of dilute sulphide ($\sim 10^{-4}$ M). In addition, the latter film exhibits enhanced barrier properties against electrolyte penetration. This conclusion can be drawn by comparing the voltammograms for both types of coated Pt electrodes in 0.1 M Na_2CO_3 (Figure 2(a), (b)), since that corresponding to the film formed in the presence of sulphide features complete blocking of the substrate active sites (Figure 2(b)). The much lower permeability of that kind of film is reached provided that a potentiodynamic protocol of synthesis is carried out. Instead, a coating generated in the presence of sulphide after a two-minute potentiostatic polarisation at 1.3 V showed the poorest barrier properties of all three polyphenol films (Figure 2(c)).

Figure 2. Voltammetric behaviour in 0.1 M Na_2CO_3 of a Pt electrode coated with a polyphenol film electrogenerated after: (a) 25 scans cyclic voltammetry in 6×10^{-2} M phenol + 0.1 M Na_2CO_3 ; (b) 25 scans cyclic voltammetry in 6×10^{-2} M phenol + 10^{-4} M Na_2S + 0.1 M Na_2CO_3 ; (c) two-minute potentiostatic polarisation at 1.3 V in 6×10^{-2} M phenol + 10^{-4} M Na_2S + 0.1 M Na_2CO_3 . A cyclic voltammogram of a clean Pt electrode (dashed line) is superimposed for comparison.

XPS Measurements

The scrutiny of the elemental composition of the polyphenol coatings obtained under the three dissimilar experimental conditions described above were carried out by XPS surface analysis. These experiments were envisaged to find out whether the incorporation of additional chemical substituents within the polymeric matrix, rather than mere structural changes, were at the origin of the different barrier properties.

Figure 3 shows the C1s spectra for polyphenol films obtained as indicated in Figure 2. In all three cases, the C1s feature can be deconvoluted into two distinct components with core-level BEs at 284.2–284.6 and 285.6–286 eV (see Table I). The major C1s peak can be associated with unfunctionalised aromatic carbons within phenolic rings.^{21,22} The minor C1s peak shows a positive binding energy shift of 1.3–1.4 eV from the main contribution, which is close to the average chemical

Table I. Binding energies of C1s, O1s, S2p, and Pt4f levels for polyphenol electropolymerised on Pt films electrodes

PPO sample	Polymerisation conditions	C1s	O1s	S2p	Pt4f _{7/2}
1	Potentiodynamic/no solution sulphide	284.3	531.1	—	71.1
		285.7	533.0	—	72.2
2	Potentiodynamic/solution sulphide	284.2	531.0	163.8	71.0
		285.6	532.9	—	72.0
3	Potentiostatic/solution sulphide	284.6	531.8	—	71.2
		286.0	533.0	—	72.5

Figure 3. C1s XPS spectra of polyphenol coatings electropolymerised on Pt as stated in: (a) Figure 2 (a); (b) Figure 2 (b) and (c) Figure 2 (c).

shifts found for C–O–C and C–OH functional groups.²¹ Thus, the C1s spectrum in Figure 3 is fully consistent with the existence of ether-type bonds between aromatic rings expected for polyphenol films, in agreement with previous FT-IR studies.^{8, 13, 18} It should be emphasized the absence of any feature attributable to –C=O (usually shifted by +2.90 eV relative to the main carbon peak²¹), which allows to discard the formation of quinone-type structures in the polymer.

The O1s spectra are shown in Figure 4. For the polymer coatings generated potentiodynamically (Figure 4 (a), (b)), the O1s signal can be satisfactorily fitted with a contribution at 533 eV, accompanied by a weak feature at 531 eV (Table I). The position of the former

Figure 4. O1s XPS spectra of polyphenol coatings electropolymerised on Pt as stated in: (a) Figure 2 (a); (b) Figure 2 (b) and (c) Figure 2 (c).

peak is close to the mean BE exhibited by ether bonds between aromatic carbons, 533.25 eV, but it cannot be unequivocally distinguished from hydroxyl groups attached to benzene rings with a slightly higher BE of 533.6 eV.²¹

The XPS analysis also probed the composition of the platinum substrate. The Pt4f spectrum (not shown) is composed of a primary unshifted doublet with the 7/2 component at around 71 eV and a minor doublet with a Pt4f_{7/2} peak at about 72 eV (Table I). These signals correspond to Pt atoms in the metallic state and Pt atoms in a +2 oxidation state respectively.²³ The O1s level at 531 eV points that Pt⁺² is in the form of a surface platinum hydroxide.²³ For a polyphenol film generated after potentiostatic polarisation at 1.3 V in the

presence of sulphide (Figure 4(c)), the O1s level increases in intensity relative to the peak at 533 eV and shifts to higher binding energies, yet still remaining within the range reported for transition metal hydroxides, 531.5 ± 0.5 eV.²³ This behaviour can be related to the growth of a thicker surface oxidized Pt film under potentiostatic conditions.

The detection of the substrate Pt core levels allows a rough estimate of the maximum thickness of the polyphenol films to be made, assuming that the coating was uniformly built up. The mean thickness should be lower than about three times the escape depth of the Pt4f photoelectron through the polymeric material.²¹ From a escape depth of 3.3 nm (based on polystyrene and bakelite²⁴) a maximum thickness of ~ 10 nm is obtained. This thickness is within the order of magnitude of ultrathin polyphenol films formed on Au from tetramethylammonium phenoxide in acetonitrile (5–7 nm).⁹ Moreover, a typical sampling depth of 7.3 nm (at normal take-off angles) has been reported for the C1s level in polymeric materials when excited by MgK α .²¹ From these two lengths, one can conclude that XPS is likely to be probing the average elemental composition of the whole film.

The photoelectronic spectral range encompassing the S2p core levels was also studied for our three types

of polymeric films (Figure 5). As expected, sulphur was not detected within polymers synthesized in the absence of solution sulphide (Figure 5(a)), whereas a very weak signal centred at 163.8 eV was observed in polyphenol films formed in its presence (Figure 5(b)). Curve fitting with S2p_{3/2, 1/2} doublets was not attempted due to the weakness of the signal and the relatively low signal-to-noise ratio. At this point, the oxidation state of sulphur could not be determined exactly, although oxygenated sulphur species, with binding energies higher than 165 eV,²⁵ can be confidently excluded. A more detailed discussion on the chemical nature of sulphur will be given further below. The spectrum in Figure 5(b) demonstrates unequivocally that sulphur is incorporated within the polymeric matrix, but this seems only to take place when the electropolymerisation is conducted by cyclic voltammetry, since XPS spectra for polyphenol films created potentiostatically did not show any clear S2p level signal (Figure 5(c)). Thus, it seems that the inclusion of sulphur is favoured when multiple potential scanning involving oxidation and reduction processes is imposed.

The atomic composition of the three types of polyphenol films can be inferred from integration of the relevant XPS signals. These data are given for the polymer elemental constituents (C, O, and S) in the form of atomic percentages and atomic content relative to the total amount of carbon (Table II). From these data it follows that those films grown potentiodynamically show a similar O/C ratio, thus possessing a similar average number of ether-type bonds and/or hydroxyl groups per benzene ring. Moreover, the O/C ratio is higher than that expected for a linear polyphenol film (1/6, equivalent to one oxygen atom per benzene ring) and also higher than those reported earlier for polyphenol films deposited under a variety of conditions.^{11, 14} On the contrary, the film built up under potentiostatic conditions does exhibit an O/C content close to the theoretical 1/6. Branching to a certain extent can be posed at the origin of the high oxygen content in polymers 1 and 2, yet the presence of some amount of hydroquinone-type moieties should not be ruled out.

A more refined view of the structure of the films can be postulated after considering the ratios of the integrated intensity of the ~ 286 eV C1s peak (accounting for carbon bonded to either ether oxygen atoms or hy-

Figure 5. S2p XPS spectra of polyphenol coatings electropolymerised on Pt as stated in: (a) Figure 2 (a); (b) Figure 2 (b) and (c) Figure 2 (c).

Table II. Elemental composition of polyphenol films electropolymerised on Pt electrodes as deduced from XPS data

PPO sample ^a	% C	% O ^b	% S	O/C	S/C	C-OR/C	O/C-OR	C/Pt
1	79.7	20.7	0	0.26	0	0.33	0.79	32.0
2	80.1	19.6	0.3	0.24	0.004	0.37	0.66	31.2
3	85.6	14.4	0	0.17	0	0.28	0.61	11.0

^aPolymerisation conditions as indicated in Table I. ^bO1s peak at 533 eV.

droxyl groups and henceforth denoted C–OR) to the total carbon integrated intensity and that of the 533 eV O1s peak to the C–OR peak (Table II). In all three cases, the C–OR/C ratio is close to 1/3 (*i.e.*, two ether or hydroxyl carbons per benzene ring). This figure is that theoretically expected for a linear polyphenol polymer, but it can also be accounted for the existence of hydroquinone-type structures. Furthermore, the ratio of the 533 eV O1s peak to the C–OR peak lies between 0.5 (the expected value when all oxygen atoms are involved in C–O–C bonds) and 1 (for oxygen belonging to C–OH functionalities). This fact suggests that excess oxygen is mainly due to the presence of hydroxyl groups rather than branching. The O/C–OR ratio exceeds 0.75 for polymer 1, thus indicating that more than 50% oxygen atoms participate in OH groups. By contrast, the 533 eV O/C–OR ratio is closer to 0.5 for polymer 2 and 3, thus suggesting a prevalence of ether-type oxygen. The prevalence of ether-like oxygen over hydroxyl oxygen occurring in polyphenol films formed in the presence of sulphide when compared to those formed in sulphide-free solution is consistent with our previous spectroscopic data,¹⁸ in which a decrease in the OH/COC integrated band intensity ratio was observed for sulphur-containing polyphenol when compared with sulphur-free polyphenol.

Finally, a brief discussion on the C/Pt ratio is pertinent. This ratio may well be taken as an account of the total amount of polymer deposited on the Pt surface, and hence as an estimate of the polymer thickness. Basing on this figure, it appears clear that the polymeric films formed under potentiodynamic conditions possess a comparable thickness, which is nearly three times higher than the thickness of the film generated at a constant anodic potential. Overall, it can be suggested that the poor barrier properties shown by this latter polymer (see Figure 2(c)) are a consequence of inefficient potentiostatic electropolymerisation conditions, which yield thinner films and, when formed in the presence of solution sulphide, are unable to bring about the incorporation of sulphur atoms within the polymeric matrix.

Compositional changes of polyphenol films formed in the presence of sulphide.

The compositional changes occurring at the first stages (*i.e.*, during a single voltammetric cycle) of the formation of a polyphenol film in the presence of solution sulphide were monitored with the aid of XPS. This study was accomplished by emersing the electrode sample at a selected potential during a single voltammetric cycle 0.3 → 1.5 → 0.3 V/RHE. After emersion, the Pt sample was rinsed thoroughly with ultrapure water, dried under a N₂ stream and submitted to XPS anal-

Table III. Binding energies of deconvoluted S2p_{3/2} level as a function of the emersion potential for polyphenol films generated in a single voltammetric sweep

Emersion potential (V/RHE)	S2p _{3/2}			
	Environment 1		Environment 2	
	BE (eV)	%	BE (eV)	%
1.15 ^a	162.2	93.98	164.4	6.02
1.25 ^a	162.3	94.90	164.3	5.10
1.30 ^a	162.2	91.5	164.8	8.5
1.40 ^a	162.3	89.78	165.2	10.22
0.30 ^b	162.4	86.84	166.2	13.16

^aSample emersed in the forward scan. ^bSample emersed in the reverse scan.

ysis. Selected emersion potentials were 1.15 V (before the main voltammetric peak in Figure 1, dashed line), 1.25 V (at the voltammetric peak), 1.3 V (immediately after the voltammetric peak), 1.4 V (after the main peak was fully traversed) and 0.3 V (after the completion of the cycle). In all cases, the C, O, and Pt XPS signals (not shown) display the same features already described above and barely change with the emersion potential during the first voltammetric cycle. It follows that a film with aromatic ring backbone and ether/hydroxyl functionalities is being built up from the very first sweep.

The S2p photoelectronic spectra of the polyphenol film formed up to every emersion potential are drawn in Figure 6(a)–(e). Regardless of the emersion potential, a major doublet appears with the 2p_{3/2} component at a mean BE of 162.3 eV (see Table III). This doublet accounts for ~90% of the total S2p intensity. The 2p_{3/2} component of the minor doublet (Table III) remains near 164 eV for spectra in Figure 6(a), (b) and shifts progressively up to higher binding energies for spectra taken at emersion potentials above 1.25 V and after the completion of the voltammetric cycle (Figure 6(c)–(e)). This latter peak can be readily associated with small amounts of elemental sulphur (S8)²⁵ codeposited within the polymeric film. At high potentials, the shift of the photoelectronic peak to BEs above 165 eV indicates the occurrence of high-oxidation state sulphur, which probably proceeds from the conversion of deposited elemental sulphur into oxy-sulphur species²⁵ that are retained within the polymeric material.

The BE of the major doublet is higher than that for atomic sulphur adsorbed on metallic substrates, usually close to 161 eV.^{26–33} Rather it matches fairly well with that found for multilayers of sulphur deposited on Au after oxidation of sulphide at pHs ranging from acidic to highly alkaline.^{30, 34–37} Moreover, a photoelectronic core level at 162.4 eV was found in the spectra of Pt samples emersed at various potentials (0.8, 1.1, and 1.3 V) during a potential linear sweep from 0.0 to 1.5

Figure 6. S2p XPS spectra of polyphenol films formed on Pt as a function of the emersion potential along a single voltammetric cycle ($0.3 \rightarrow 1.5 \rightarrow 0.3$ V) in 6×10^{-2} M phenol + 10^{-4} M Na_2S + 0.1 M Na_2CO_3 : (a) 1.15 V; (b) 1.25 V; (c) 1.30 V; (d) 1.40 V and (e) 0.3 V after completion of the cycle.

V/RHE run in a 10^{-4} M Na_2S + 0.1 M Na_2CO_3 solution free of bulk phenol (Figure 7). The peak at 162.4 eV in Figure 7(b) corresponds to a sulphur layer formed on the Pt surface, which is responsible for the strong blockage of the hydrogen adsorption/desorption sites observed in the voltammogram of Figure 7(a). Thus, it can be concluded that the main sulphur species present the polymer is of the same nature than that formed by oxidation of sulphide on Pt or Au electrodes in the absence of monomer, and alternative assignments, like the occurrence of thiolate groups attached to phenylene

Figure 7. (a) First cyclic voltammogram of a Pt electrode in 10^{-4} M Na_2S + 0.1 M Na_2CO_3 . (b) S2p XPS spectra of a sulphur layer formed on Pt as a function of the emersion potential.

moieties and coordinated to surface Pt atoms,^{38,39} seem improbable. The other two signals appearing in Figure 7(b), at 165–166 and 168 eV, can be attributed to oxygenated sulphur species, like SO_x species or sulphites which are known to show energies in the range 165–168 eV²⁵ and sulphates, with binding energies at about 168–169 eV.²⁵ These species may derive from partial oxidation of surface sulphur and, to some extent, from oxidation of bulk sulphide.

In summary, results in Figures 6 and 7 suggest that the polymeric film obtained after a single cycle in a

Table IV. Compositional changes of S-polyphenol composite films as a function of the emersion potential along a single voltammetric cycle

Emersion Potential (V/RHE)	C/Pt	C-OR/C	S/C
1.15 ^a	0.908	0.413	0.199
1.25 ^a	1.582	0.378	0.140
1.30 ^a	2.516	0.379	0.098
1.40 ^a	6.526	0.374	0.025
0.30 ^b	11.722	0.345	0.037

^aSample emersed in the forward scan. ^bSample emersed in the reverse scan.

solution containing both phenol and sulphide could mainly be regarded as a composite material formed by the simultaneous deposition of sulphur and polyphenol chains. Deposited sulphur may act as an efficient filler of the pores and pinholes that an otherwise S-free polyphenol film tends to present and hence a more densely packed material is obtained. This fact can contribute the observed enhancement of the film barrier properties. Also, a synergistic effect arising from the inherent insulating properties of the polyphenol fraction and from the well-documented inhibiting properties of sulphur layers³⁶ may be invoked.

Finally, it is worth discussing the quantitative compositional changes suffered by the S-polyphenol composite film as a function of the emersion potential along a single voltammetric cycle. Relevant data for S, C, and Pt are expressed in Table IV as relative ratios. The S/C ratio decreases significantly as the potential is increased in the forward direction to yield a lowest value at the positive end of the voltammogram (*i.e.*, under overoxidation conditions). Instead, it stays comparatively unchanged on sweeping back to 0.3 V. The main reason for the observed decrease seems not to be a loss of sulphur by oxidation, but the increase in the amount of polymer carbon, *i.e.*, the thickening of the polyphenol fraction of the film, that takes place along a single voltammetric cycle. This contention is substantiated by the sharp rise of the C/Pt ratio measured both in the forward and the reverse sweeps (Table IV). These data suggest that the incorporation of sulphur in the composite material occurs principally at the early stage of filming and successive polyphenol layers gradually impoverished in sulphur develop upon cycling. This assumption would explain the low S/C ratio encountered in the films generated after 25 cycles (see Table II, sample 2). By contrast, the C-OR/C ratio undergoes a small variation throughout a cycle and remains close to the value obtained for the film formed after 25 cycles. Therefore, the amount of ether-type links per benzene ring is essentially constant during the growth of the film and is barely affected by the presence of sulphur within the

polymeric matrix.

CONCLUSIONS

As disclosed by XPS surface analysis, polyphenol films electropolymerised from phenol on Pt in sodium carbonate medium are compounded of an aromatic ring backbone linked by ether-type bonds and with some hydroxyl groups. The films formed potentiodynamically in the presence of solution sulphide contain incorporated sulphur in a small percentage. Sulphur within the film is characterised by a 2p_{3/2} core level at 163.2 eV. This BE is also observed for a sulphur layer deposited onto Pt from sulphide in the absence of phenol. Thus, the film could be described as a sulphur-polyphenol composite material. The evolution of the S/C ratio along a single cycle and the comparison with values achieved after 25 scans suggest that the incorporation of sulphur occurs mainly at the early stages of filming and an enrichment in the polyphenol fraction takes place as the film thickens with successive cycling. The polymeric fraction maintains the amount of ether-type links per benzene ring basically constant during growth.

The S-polyphenol composite film exhibits enhanced barrier properties over polyphenol films formed in the absence of sulphide. A synergistic combination of the inhibiting properties of the sulphur and the polyphenol fractions and/or a higher packing density (*i.e.*, lower porosity and increased resistance to electrolyte penetration) can be argued to explain this behaviour. The presence of sulphur seems not to effect drastic structural changes in the polymeric fraction, which exhibits a similar C-OR/C and C/Pt (*i.e.*, mean thickness) ratios than polyphenol formed in the absence of sulphur. On the contrary, polyphenol films formed potentiostatically in sulphide-containing solutions show no incorporated sulphur and a lower C/Pt ratio (*i.e.*, thinner films), which are likely to be at the origin of their poor barrier properties.

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