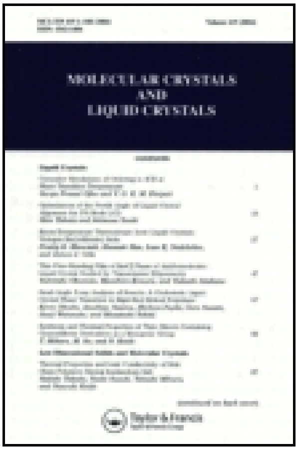

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electropolymerization Mechanism and Electrochemical Behaviour of Poly(o-phenylenediamine) film Synthesized in the Presence and Absence of some Surfactants

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Version of record first published: 18 Oct 2010

To cite this article: V. Brânzoi, Luisa Pilan & Florina Brânzoi (2004): Electropolymerization Mechanism and Electrochemical Behaviour of Poly(o-phenylenediamine) film Synthesized in the Presence and Absence of some Surfactants, Molecular Crystals and Liquid Crystals, 416:1, 61-72

To link to this article: http://dx.doi.org/10.1080/15421400490482899

Mol. Cryst. Liq. Cryst., Vol. 416, pp. 61/[317]–72/[328], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490482899

ELECTROPOLYMERIZATION MECHANISM AND ELECTROCHEMICAL BEHAVIOUR OF POLY(O-PHENYLENEDIAMINE) FILM SYNTHESIZED IN THE PRESENCE AND ABSENCE OF SOME SURFACTANTS

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O-Phenylenediamine was electropolymerized on copper electrodes by means potentiodynamic method. The electrochemical properties of poly(o-phenylenediamine) films electrosynthesized from aqueous solutions containing different anions were studied by cyclic voltammetry and spectroscopy. The results indicate that the mechanism of the redox process is complex and may be governed by the diffusion of the cations and anions of the electrolyte. The kinetics of the processes can be monitored by changing the nature of the electrolyte and this may allow modulation of the electrical and optical properties of poly(o-phenylenediamine) (POPD) films.

The polymer film consisted of more than two components. Among those, only one component was active in oxygen reduction, which was formed mainly in the earlier stage of the electropolymerization. It was suggested that the active polymeric component has a structural unit similar to the cyclic dimer (2,3-diaminophenazine). Finally, the electropolymerization mechanism for the formation of the active and inactive components has been proposed.

Keywords: current peak; cyclic voltammogram; diffusion current; energy barrier; kinetic parameters; scan rate

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INTRODUCTION

Copper and its alloys are applied extensively in marine environment due to their high corrosion resistance in harsh seawater. In addition, copper dissolution in chloride solution is very important in the electropolishing and electromachining industries. Such as, the electrochemical behaviour of copper in neutral aqueous solutions containing chloride ions has been extensively studied in relation to the formation and properties of passivating layers in relation to the metal corrosion resistance. Even if copper corrosion in near neutral aqueous solutions seems to be low, the damage from the corrosion products such as Cu^{2+} ions could be very harmful. In most cases of copper corrosion, an additive must be added to the environment in order to modify or hinder the reactions involved in process. Theoretically, there are a great number of materials that could be applied as corrosion inhibitors for copper corrosion, but only a few formulations have been thoroughly investigated [1–7]. Azoles, specifically triazoles, have been intensively investigated as effective copper corrosion inhibitors.

Nowadays, the synthesis and chemical, physical and electrical properties of π-conjugated polymers are subjects of recent interest. Much of the research on such system focuses on their basic electrical properties and on their connection to a variety of potential applications. The ladder-type polymers such as poly(o-phenylenediamine) and poly(o-aminophenol) have been electrochemically prepared and their possible applications to electron transfer mediators for oxygen reductions, pH sensitive electrodes, electrochemical diodes, corrosion inhibitors and permselective detection of anions have been sought.

It is found that some polymers such as: polyaniline (PANI), polypyrrole (PPY), poly-o-phenylenediamine (POPD) could either enhance the corrosion rate or produce significant corrosion protection depending on the chemical nature of the polymer backbone and the condition in which the material is processed and doped. These polymers are found to adhere well to the metal surface and provide exceptional protection both under an applied potential and at elevated temperature.

EXPERIMENTAL

Effects of the organic additions were studied through tracing the polarization curves, calculation of the kinetic parameters (electrochemical parameters) in case of solutions with organic compounds, especially the current densities, and their comparison with the kinetic parameters of the solution without organic compounds. The used organic compounds were o-phenylenediamine and hexadecyl trimethyl ammonium chloride.

The working electrode made of copper had a surface of 0.2 cm^2. In all experiments the electrochemical polarization was started about 30 minutes after the working electrode was immersed in solution, to allow the stabilization of the stationary potential. The working electrode potential was always measured with reference to the saturated calomel electrode and was plotted vs. the current in external circuit, obtaining the anodic or cathodic curves according to the variation electrode potential. Before each measurement the working electrode was polished with fine emery, then it was immersed in boiling benzene for five minutes to remove the remaining fat traces and abrasive dust on the electrode after polishing. After polishing, the working electrode was washed with distilled water and inserted in the polarization cell, which was the usual three-electrode type.

RESULTS AND DISCUSSION

Figure 1 shows the anodic polarization curve of copper in 1 M NaCl solution without addition of organic compound. The potentiogram shows four

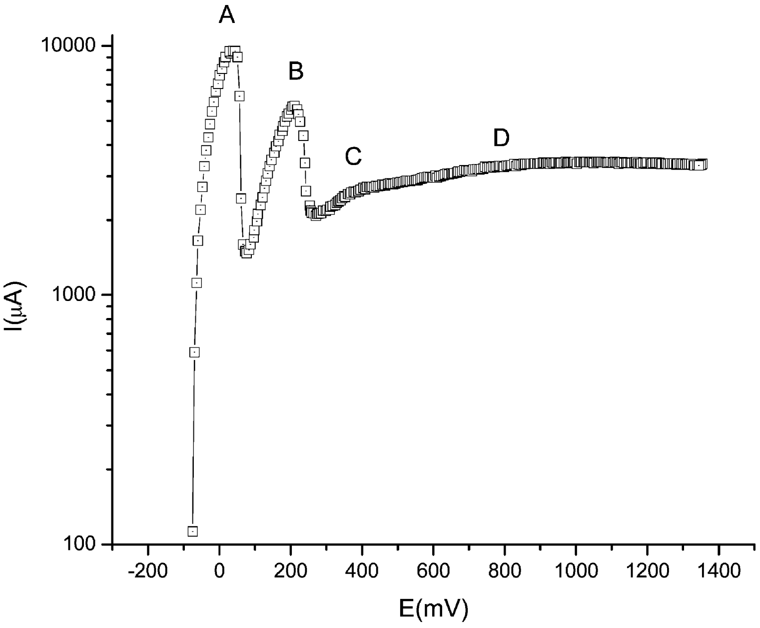

FIGURE 1 The potentiogram of copper electrode in 1 M NaCl aqueous solution at 25°C.

anodic peaks and a Tafel region at lower overvoltages. In the Tafel region the anodic dissolution of copper takes place and the process of dissolution is controlled by activation. The first maximum of current is due to the anodic oxidation of copper. For this first oxidation peak (A) we consider the following mechanism:

the adsorption of the aggressive anion Cl^- on the electrode surface

$$Cu + Cl^- \rightarrow CuCl^-_{ads} \tag{1}$$

the electrochemical step (copper dissolution)

$$CuCl^-_{ads} \rightarrow CuCl + e^- \tag{2}$$

another adsorption step of Cl^-

$$CuCl + Cl^- \rightarrow CuCl^-_{2\,ads} \tag{3}$$

The decreasing region of peak (A) is due to formation CuCl that is a white precipitate and forms a protective film on the electrode surface.

The second anodic peak corresponds to the following mechanism:

$$CuCl^-_{2\,ads} \rightarrow Cu^{+2} + 2Cl^- + e^- \tag{4}$$

$$Cu^{+2} + H_2O \rightarrow CuO + 2H^+ \tag{5}$$

$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^- \tag{6}$$

The ascendent region of the peak B corresponds to the reaction (4) and the descendent region to the formation of CuO and Cu_2O according to Pourbaix diagram.

Finally, we consider that the anodic oxidation peaks C and D corresponds to the following reactions (according to Pourbaix diagram):

$$Cu_2O + 2OH^- \rightarrow 2CuO + H_2O + 2e^- \tag{7}$$

$$Cu_2O + H_2O \rightarrow 2CuO + 2H^+ + 2e^- \tag{8}$$

Analysis of the polarization curve from Figure 1 shows that, at the low overvoltages, the Tafel relation is met indicating that both the anodic and the cathodic reaction are controlled by activation. On the anodic polarization curve this could be explained by the presence of aggressive anions (Cl^-) which prevents the formation of the passive film and accelerates the process of anodic dissolution, the more, the greater is the concentration of the chloride ion (see Table 1). It is assumed that halogen ion participates by competitive adsorption in the reaction on the metal – electrolyte interface which forms chemisorbed films that satisfy the surface affinity for oxygen atoms

TABLE 1 The Kinetic Parameters of Copper Electrode Determined from the Polarization Curves in Different Aqueous Solutions of NaCl at a Scan Rate of 5 mV·s^{-1} and 25°C

Solution	Ip_A (μA)	Ip_B (μA)	Ip_C (μA)	Ip_D (μA)	$I_{L,D}$ (μA)
0.25 M NaCl cycle 5	1689.4	6442.8	1345	1650	3771.7
0.50 M NaCl cycle 5	5592	4478.3	1981.8	2111.6	1920
0.75 M NaCl cycle 5	8159.5	3896	2307	3096.1	2806
1M NaCl cycle 5	9191.6	3049.6	2043.6	3901.3	3566

or water molecules. The specific adsorption of Cl^- anions reduces the potential energy barrier necessary for transition from the metal phase in solution.

At high overvoltages, a limit diffusion current appears on the anodic and cathodic polarization curves, suggesting that at higher densities of current, the aggressive anions transport on the electrode surface gradually becomes rate-determinant (concentration polarization). Mass transfer effects have been shown to be significant during the anodic dissolution of copper in

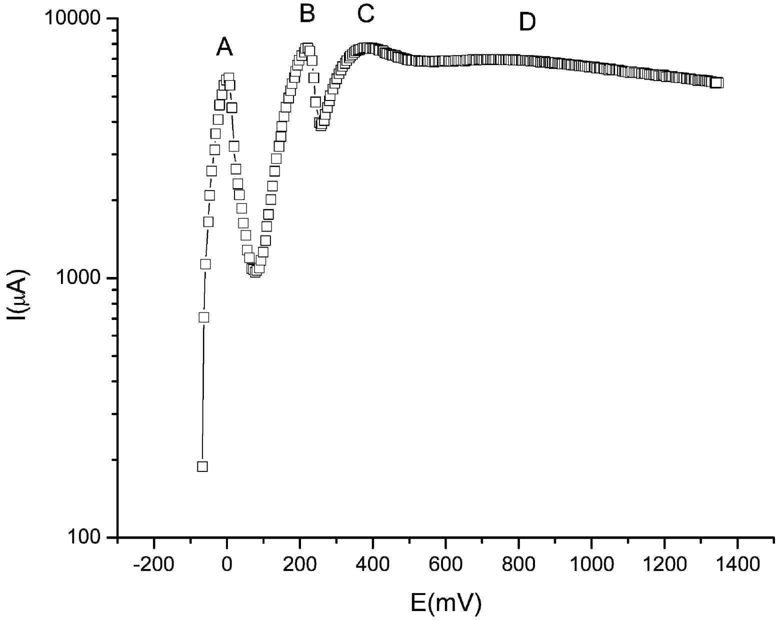

FIGURE 2 The potentiogram of copper electrode in 1 M NaCl + 0.01 M o-phenylenediamine aqueous solution at 25°C.

chloride media with cuprous chloride complexes as major product species. Several mechanisms involving reactions (2) and (3) and mass transfer of $CuCl_2^-$ from the electrode surface to the bulk solution have been suggested to explain the kinetics of copper dissolution in the apparent Tafel region.

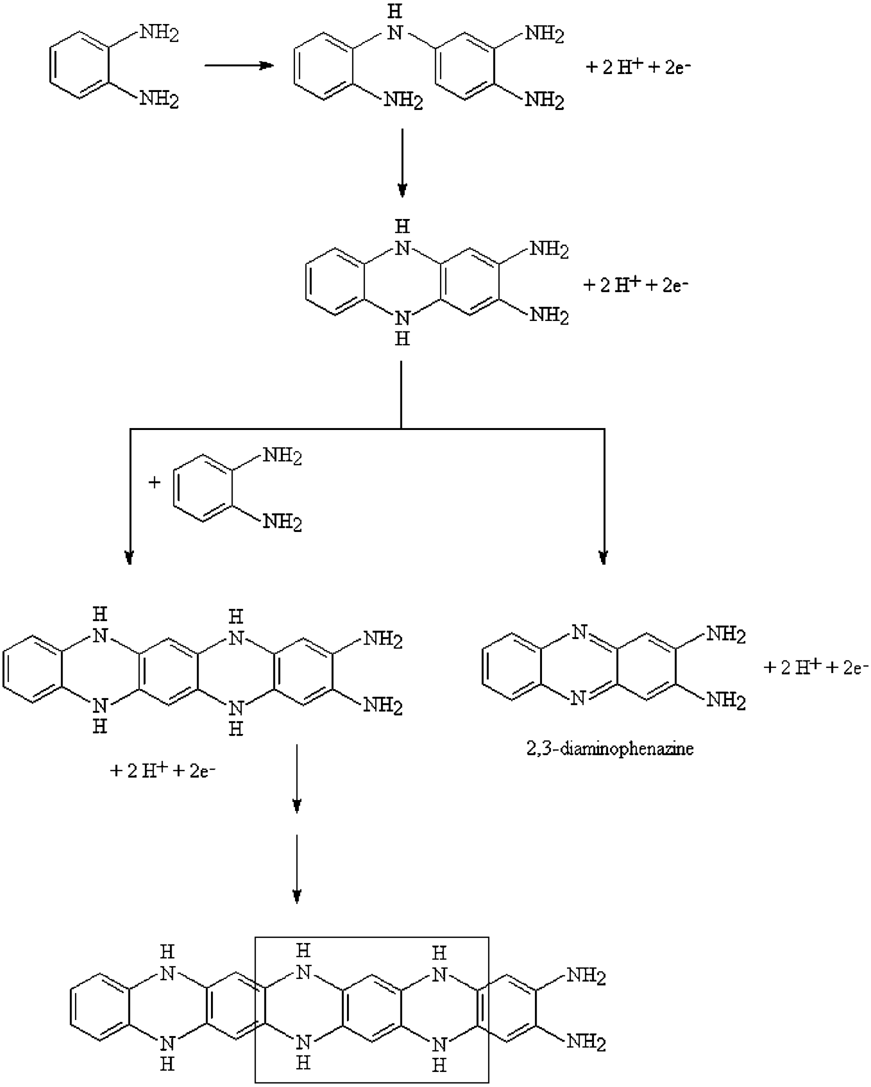

FIGURE 3 Polymerization mechanism of o-phenylenediamine.

Further, we studied the anodic polarization behaviour of copper electrode in aqueous solution of 1 M NaCl with 0.01 M o-phenylenediamine. The addition of o-phenylenediamine led in all cases to a drastically decreasing of the first anodic peak and this fact we explained in the following way: o-phenylendiamine is an organic compound with nitrogen atoms in its molecule, hence it is an adsorption inhibitor which adsorbs strongly on

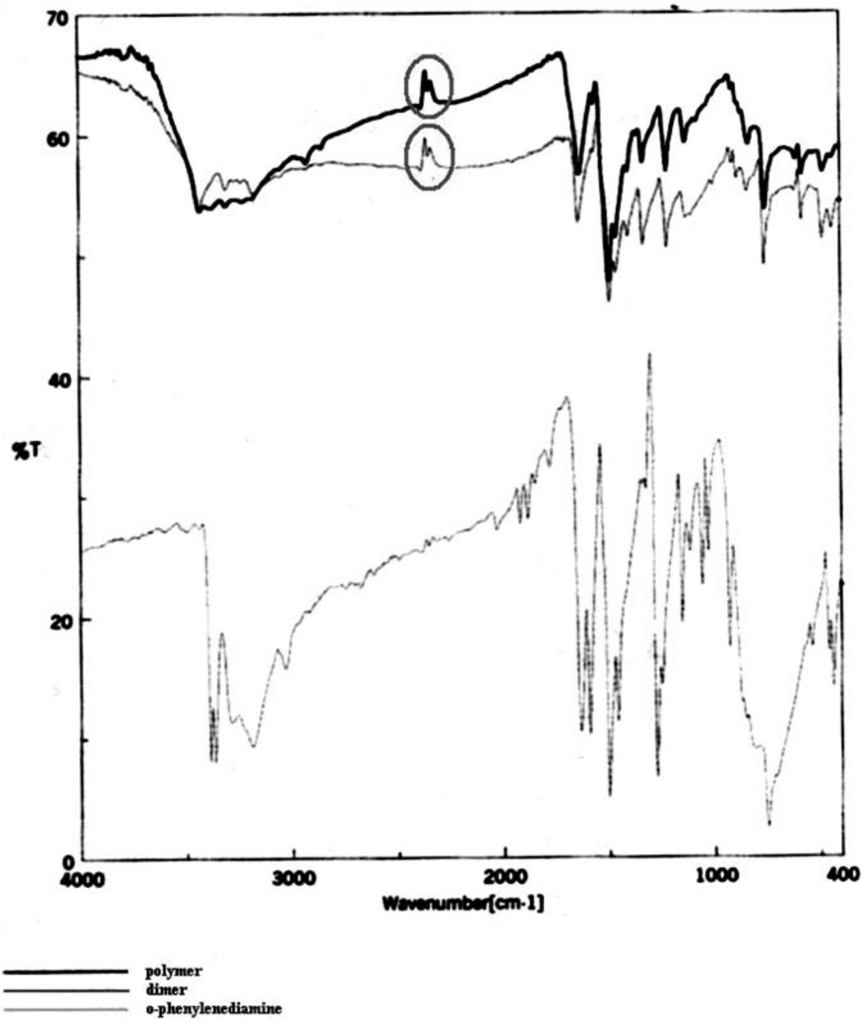

FIGURE 4 IR spectra of o-phenylenediamine, its dimer and poly(o-phenylenediamine).

the electrode surface and hinders the anodic dissolution of copper. Consequently the current decreases, as we see in Figure 2.

Further, at the potential scan in anodic direction, a second anodic peak appears. This peak is higher than peak B from Figure 1. This increasing of peak B we explained considering that, at this potential, both anodic oxidations of copper and o-phenylenediamine takes place. The main process in this case we consider that is the anodic oxidation of o-phenylenediamine to its dimer (see Fig. 3).

The formation of the dimer was pointed out by UV-VIS and IR spectra (Figs. 4 and 5) and by formation of a red precipitate that forms in the solution volume and on the electrode surface.

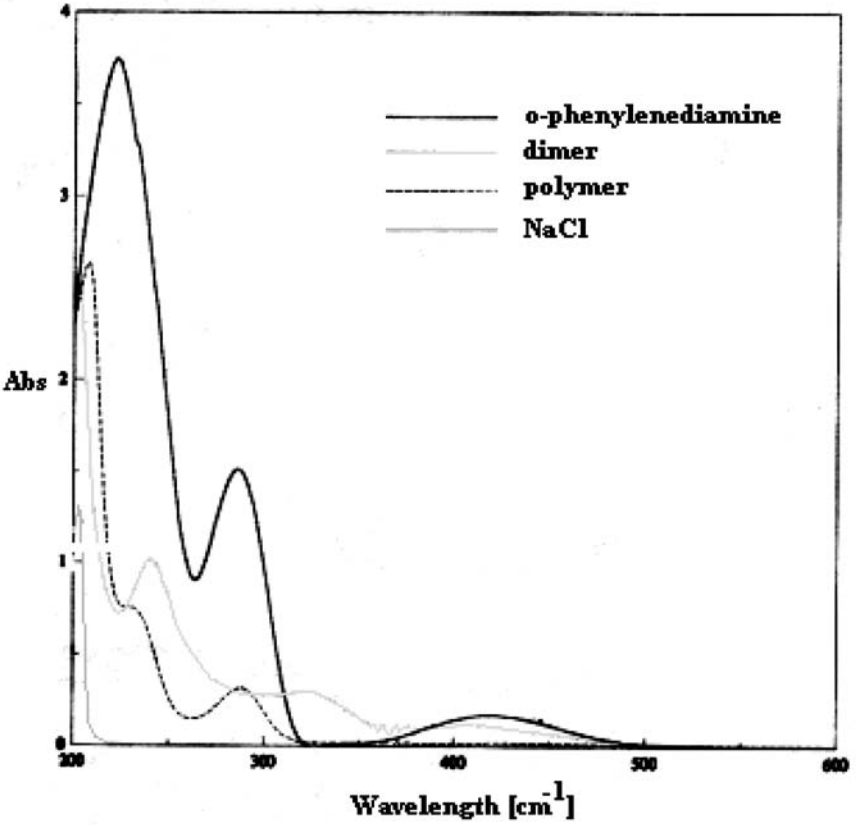

FIGURE 5 UV-VIS spectra of o-phenylenediamine, its dimer and poly(o-phenylenediamine).

The increase of the currents corresponding to peaks C and D we presume that takes place due to further anodic oxidation of o-phenylenediamine dimer with formation of poly(o-phenylenediamine) according to the mechanism presented in Figure 3.

Cyclic voltammetry of the POPD-film coated copper electrode was carried out in aqueous solution of 0.1 M NaCl saturated with oxygen to examine its catalytic activity in oxygen reduction. In Figure 6 is presented the cyclic voltammogram of the copper electrode in aqueous solution of 0.1 M NaCl. The cathodic current peak (C) located at –0.15 V vs. SCE can be identified as the oxygen reduction current.

Figure 7 shows the cyclic voltammogram of the copper electrode in aqueous solution of 0.1 M NaCl with addition of 0.01 M o-phenylenediamine. This voltammogram shows an enhanced cathodic current at about –0.25 V vs. SCE, which is identified as the polymer mediated oxygen reduction current. This illustrates that the overpotential for oxygen reduction is reduced by 100 mV by modifying the electrode with POPD. Also immediately apparent in the voltammogram from Figure 7 is that the cathodic peak current is much increased comparatively with the current peak (C) from Figure 6.

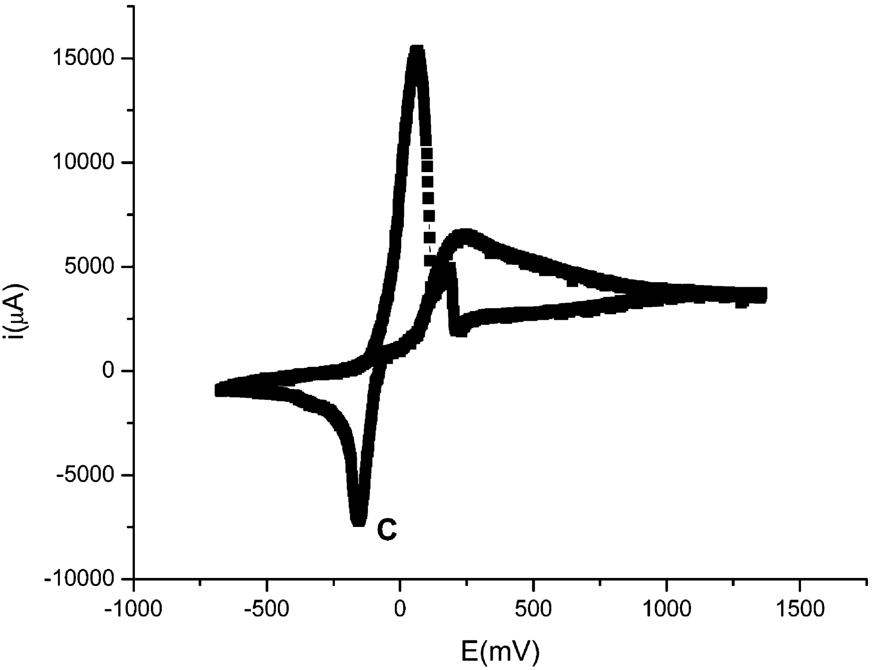

FIGURE 6 Cyclic voltammogram of the copper electrode in an aqueous solution of 0.1 M NaCl; potential scan rate: 20 mV/s at 25°C.

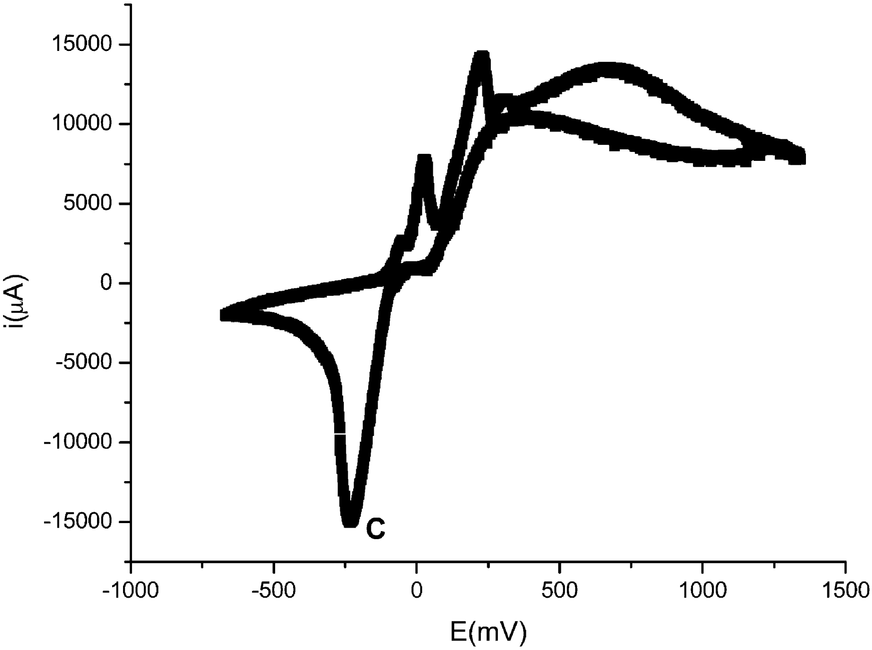

FIGURE 7 Cyclic voltammogram of the copper electrode in aqueous solution of 0.1 M NaCl with addition of 0.01 M o-phenylenediamine; potential scan rate: 20 mV/s at 25°C.

This points out that only POPD is active in the electrocatalytic O_2 reduction (see comparatively Figs. 6 and 7).

The addition of the organic compounds to the amounts shown in Tables 2 and 3 led in all cases to the inhibition of the dissolution process. In this case the inhibition is the result of the adsorption of the organic compound on the surface of the metal, forming an invisible film of a few molecules thick. The halides are the most effective derivatives as they

TABLE 2 The Kinetic Parameters of Copper Electrode Determined from the Polarization Curves in Aqueous Solutions of NaCl in Presence of o-phenylenediamine at Different Scan Rates and 25°C

Solution	Ip_A (μA)	Ip_B (μA)	Ip_C (μA)	Ip_D (μA)	I_L (μA)
1M NaCl + 0.01 M oPD 5 mV·s^{-1}, cycle 5	5669	5164.3	5327	6032.7	5216.7
1M NaCl + 0.01 M oPD 10 mV·s^{-1}, cycle 5	5801	6499	6994.6	7975.6	8171
1M NaCl + 0.01 M oPD 20 mV·s^{-1}, cycle 5	6102	7945	5723	5637	4848

TABLE 3 The Kinetic Parameters of Copper Electrode Determined from the Polarization Curves in Aqueous Solutions of NaCl in Presence of Hexadecyl Trimethyl Ammonium Chloride

Solution	Ip_A (μA)	Ip_B (μA)	Ip_C (μA)	Ip_D (μA)	I_L (μA)
1M NaCl + $0.82 \cdot 10^{-3}$ M HDTAC 5 mV·s^{-1}, cycle 5	4772	4392.4	–	–	4905.8
1M NaCl + $0.82 \cdot 10^{-3}$ M HDTAC 10 mV·s^{-1}, cycle 5	6532	2837.2	5094.4	–	9370.2
1M NaCl + $0.82 \cdot 10^{-3}$ M HDTAC 20 mV·s^{-1}, cycle 5	2949	3154	2584	–	4038
1M NaCl + $1.64 \cdot 10^{-3}$ M HDTAC 5 mV·s^{-1}, cycle 5	4203.8	2694	2643.8	–	4063.5
1M NaCl + $1.64 \cdot 10^{-3}$ M HDTAC 10 mV·s^{-1}, cycle 5	2905	2494	–	–	1761
1M NaCl + $1.64 \cdot 10^{-3}$ M HDTAC 20 mV·s^{-1}, cycle 5	1585	5419	1348	–	1303
1M NaCl + $3.27 \cdot 10^{-3}$ M HDTAC 5 mV·s^{-1}, cycle 5	1544.7	3604.5	1608.5	–	2453
1M NaCl + $3.27 \cdot 10^{-3}$ M HDTAC 10 mV·s^{-1}, cycle 5	8289	4084	2635	6864	5982
1M NaCl + $3.27 \cdot 10^{-3}$ M HDTAC 20 mV·s^{-1}, cycle 5	7624	3920	2724	5948	5602
1M NaCl + $3.27 \cdot 10^{-3}$ M HDTAC 40 mV·s^{-1}, cycle 5	7247	3754	2805	5693	5342

increase the inhibiting tendency of the positive quaternary ammonium ion by the well-known synergistic effect.

CONCLUSIONS

At the anodic potential scan, o-phenylenediamine oxidizes with the formation of a dimer (2,3 diamino-phenazine – see the mechanism presented in Figure 3);

At the advanced anodic polarization the formed dimer further oxidizes and lead to poly(o-phenylenediamine);

At the cathodic potential scan only the modified electrode copper/POPD is active in the electrocalaytic O_2 reduction (see Figs. 6 and 7).

The addition of the organic inhibitors led in all cases to inhibition of the corrosion process. It was observed that the organic compound HDTAC has the best efficiency.

In aqueous solutions of NaCl, the process of dissolution of copper is controlled by the activation at low overvoltages, while at high overvoltages is controlled by diffusion.

The anodic dissolution of copper in aqueous solutions of NaCl takes place by involving the aggressive anion Cl^- which leads in the first step to the formation of CuCl and in the second step to the formation of the complex copper ion $CuCl_2^-$.

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