Available online at www.sciencedirect.com

ScienceDirect

Electrochimica Acta 51 (2006) 6045–6050

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Electrochemical synthesis of poly(*ortho*-ethoxyaniline) from phosphoric and sulphuric acid solutions

M. Kraljić Roković[1], Lj. Duić*,[1]

Laboratory of Electrochemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, P.O. Box 177, Zagreb, Croatia

Received 5 June 2005; received in revised form 30 November 2005; accepted 22 December 2005

Abstract

The growth and nucleation mechanism of poly(*ortho*-ethoxyaniline) (POEA) are investigated by cyclic voltammetry (CV) and potentiostatic technique. It was shown that growing of POEA is faster in sulphuric acid solution compared to phosphoric acid solution. Different rate trends were obtained with the increase of switching potential. From cyclic voltammograms, it is evident that the obtained polymer has a similar behaviour to the one reported for polyaniline, but there is a difference in position of current peaks, due to the electronic and steric effects of ethoxy-group. In presence of different anions, a different nucleation mechanism was obtained. In sulphuric acid solution nucleation proceeds through 3D instantaneous nucleation under diffusion control, and in phosphoric acid solution nucleation proceeds through 3D progressive nucleation under diffusion control.

Keywords: Poly(*ortho*-ethoxyaniline); Electropolymerisation; Nucleation; Anion effect; Switching potential effect

1. Introduction

Conductive polymers are promising materials for new technological applications. One of the most interesting conductive polymers is polyaniline. Polyaniline has been extensively studied for its possible use in commercial applications such as rechargeable batteries, catalysis, corrosion protection, antistatic materials, textile industry and some other applications. To obtain conductive polymer of desirable characteristics for the particular application some substituted polyanilines were synthesised. Those polymers were synthesised, mostly, to increase the polymer solubility and thereby to increase the processability. Thus, Paoli and co-workers [1] have shown that poly(*ortho*-methoxyaniline) (POMA) is suitable for the application in electrochromic devices. Graeff et al. [2] produced field effect transistors (FET) from easily processable thin films of poly(*ortho*-methoxyaniline). Brusic et al. [3] obtained good results in corrosion protection of copper with poly(*ortho*-ethoxyaniline) (POEA) coatings, while Kilmartin et al. [4] provided corrosion inhibition of stainless steel using poly(*ortho*-methoxyaniline) coating.

In most papers on poly(*ortho*-methoxyaniline) or poly(*ortho*-ethoxyaniline), the synthesis was carried out using $HClO_4$ or HCl [1,5–7] as supporting electrolyte solutions, and in some papers H_2SO_4 was used [8,9].

In case of polyaniline, it was shown that polymerisation rate depends strongly on anion present in the supporting electrolyte [10], due to a different degree of specific adsorption of different anions on Pt electrode. Jackowska and co-workers [5,11] studied the effect of Cl^- and $ClO_4{}^-$ on electrodeposition and on electrochemical properties of poly(*ortho*-methoxyaniline), and found that the oxidation rate was higher in HCl than in $HClO_4$ solutions. Two-dimensional growth was proposed in $HClO_4$ solution, which suggests a compact structure, whereas in HCl solution a three-dimensional growth was proposed suggesting an open, fibrous structure. The IR analysis confirmed a structural similarity between poly(*ortho*-methoxyaniline) and polyaniline. Mattoso et al. [12] studied the influence of different substituents (methyl, methoxy and ethoxy) on the polymerisation rate and on the characteristics of the polymer, and they suggest that the presence of the substituent at *ortho*-position of aniline ring leads to a longer polymerisation time and to a decreased molar mass of polymer.

---

* Corresponding author. Tel.: +385 1 4597141; fax: +385 1 4597139.
E-mail address: lduic@marie.fkit.hr (Lj. Duić).

[1] ISE Member.

0013-4686/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2005.12.052

Leclerc et al. [13] and Kahol and co-workers [14] concluded that steric effects, as well as the electronic effect, of aniline substituent must be taken into account when considering conductivity of a particular conductive polymer. Pouget [15] examined POEA structure as well as charge transport through it. He proposes a new chain conformation opening larger cavities within chains, due to ethoxy-group in *ortho*-position. The aim of this work is to investigate the influence of the counter-ion on the synthesis, and on the characteristics of POEA growth; therefore, two different supporting electrolytes were used for POEA synthesis. Solutions of H_2SO_4 and H_3PO_4 were chosen since these acids are preferentially used in synthesising conducting polymer layers in studies of steel corrosion protection [16–18].

2. Experimental

All the experiments were carried out in a standard one-compartment cell. The working electrode was Pt-disc ($A = 0.07\,\mathrm{cm}^2$), the counter electrode Pt-foil ($A = 0.5\,\mathrm{cm}^2$) and Ag/AgCl ($3\,\mathrm{mol\,dm}^{-3}$ KCl) served as the reference electrode. All the potentials are referred to Ag/AgCl. Before each experiment the working electrode was polished using Al_2O_3 slurry (particle size, 0.3 μm), and washed with bi-distilled water. The experiments were carried out at room temperature ($t = 23 \pm 2\,°\mathrm{C}$).

The POEA synthesis was carried out by means of cyclic voltammetry (CV), and by a potential step polarisation. All chemicals were of high quality: *ortho*-ethoxyaniline (OEA) (Aldrich, p.a.), H_2SO_4 and H_3PO_4, both of p.a. quality. Solutions were prepared from bi-distilled water. POEA films were deposited from the solutions of $0.5\,\mathrm{mol\,dm}^{-3}$ *ortho*-ethoxyaniline using $1.5\,\mathrm{mol\,dm}^{-3}$ H_2SO_4 and $3\,\mathrm{mol\,dm}^{-3}$ H_3PO_4 as supporting electrolyte solutions. Different concentrations of acids were used to keep values of pH close, since polymerisation process is strongly influenced by pH of the solution [19]. Potentiostat/Galvanostat PAR Model 263A was used for electrochemical experiments.

The potential range of synthesis (CV) was from −200 to 1000 or 1200 mV, at the scan rate $\nu = 50\,\mathrm{mV\,s}^{-1}$. The layers of POEA of the same amount of charge ($Q_A = 16\,\mathrm{mC\,cm}^{-2}$), or of the same number of cycles (20 cycles), were synthesised. The charge, Q_A, necessary to switch poly(*ortho*-ethoxyaniline) from leucoemeraldine (LE), the reduced form of POEA, to emeraldine (EM), the oxidised form of POEA, was calculated by integrating the area under the current peak A (Fig. 1) [16].

The potentiostatic experiments were carried out by applying a conditioning potential of −200 mV during 10 s, and then applying a potential step to the selected potential value in the region between 630 and 800 mV.

3. Results and discussion

3.1. Cyclic voltammetry

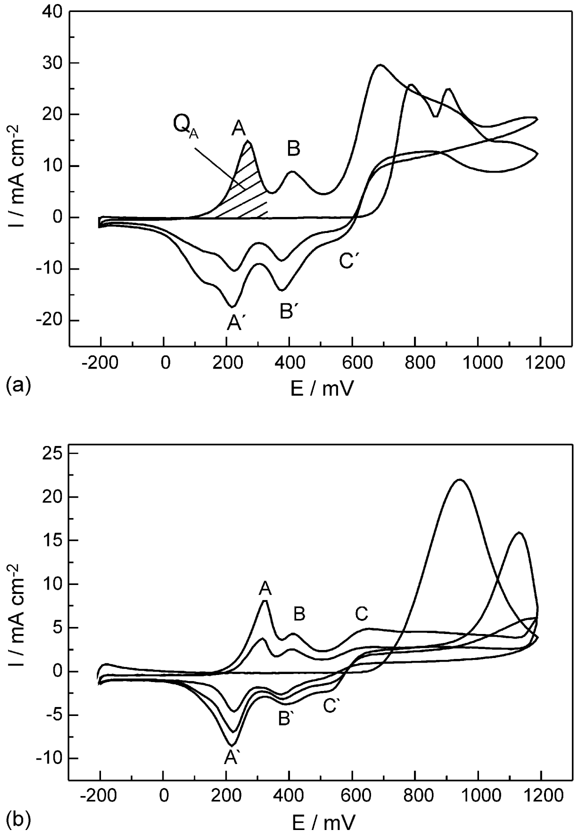

Fig. 1. (a) $POEASO_4$ layer growth; $c_{OEA} = 0.5\,\mathrm{mol\,dm}^{-3}$, $c_{el} = 1.5\,\mathrm{mol\,dm}^{-3}$ H_2SO_4 and $\nu = 50\,\mathrm{mV\,s}^{-1}$. (b) $POEAPO_4$ layer growth; $c_{OEA} = 0.5\,\mathrm{mol\,dm}^{-3}$, $c_{el} = 3\,\mathrm{mol\,dm}^{-3}$ H_3PO_4 and $\nu = 50\,\mathrm{mV\,s}^{-1}$.

Fig. 1 illustrates cyclic voltamogramms for electrodeposition of poly(*ortho*-ethoxyaniline) layer in sulphuric (a) and phosphoric acid (b) solutions. In both cases layers of approximately the same thickness were synthesised. Voltammograms in Fig. 1(a and b) show that oxidation current in the first cycle is somewhat higher in sulphuric acid solution compared to phosphoric acid solution. The anodic current is higher in the reverse scan than in the forward scan over the potential range from 700 to 600 mV in sulphuric acid solution and from 700 to 580 mV in phosphoric acid solution. That higher anodic current is the evidence for the catalytic effect of POEA which is already formed on the electrode surface. This is in accordance with the results obtained for aniline [20], *para*-phenylenediamine [21] and *ortho*-methoxyaniline oxidation [11].

During the synthesis well-developed current peaks A and B are obtained, while the current of the peak C overlaps with monomer oxidation currents. The same current peaks are registered when polyaniline is synthesised, and therefore the same redox reactions are assumed [21]. It is interesting to note that the current peak A in the forward and in the reverse scan is almost reversible, which indicates that the reduction reaction is facilitated compared to polyaniline, where the current peak A on the reverse scan is stretched over a wider potential range [10]. Considering that POEA has an ethoxy-group in *ortho*-position, i.e., an electron-donating substituent, the reduction process of polymer should be more difficult because of the higher electron density along the polymer backbone. Thus, the reversibility cannot be explained by the electronic effect of ethoxy substituent. However, it could be related to the steric effects. Namely, higher torsion angles are expected in reduced POEA compared to reduced polyaniline, which might cause a shift in oxidation potential [13]. In the forward scan it appears that electronic effects are compensated by steric effects, and there is no shift in the potential of the current peak A compared to polyaniline. However, in the reverse scan the reduction process proceeds more easily compared to polyaniline, because in leucoemeraldine form there is a torsion angle that is energetically more favourable for POEA.

However, the current peak A for POEASO4 in the reverse scan is composed of two separate peaks (Fig. 1(a)), indicating two separated electron transfers, meaning that the second electron transfer proceeds well after the potential of the first one. This actually suggests that the electronic effect of the ethoxy-substituent hinders the second electron transfer and shifts it to more negative potentials. Namely, when the electrode was held at the potential of 240 mV (during 35 min) and after that cycled to more negative potentials, only one well-defined peak (the second peak) was obtained. This suggests that there is a relatively stable state of POEA which exists between emeraldine and leucoemeraldine state. It is assumed that such a state is of a protoemeraldine oxidation level, which lies between leucoemeraldine and emeraldine oxidation states.

To resolve the peak C of POEASO4 layer, potential cycling in sulphuric acid solution (Fig. 2) at scan rate $\nu = 2\,\mathrm{mV\,s^{-1}}$ was applied. It is evident that the potential of the current peak C is less positive than the one obtained for polyaniline [22]. This potential shift is explained by the electronic effect of ethoxy-substituent. Such potential shift is in accordance with the previous results where synthesis of poly(alkyl-aniline) and poly(alkoxy-aniline) was carried out [13,6]. However, it is evident that the current peak C is much smaller than the current peak A. If the polymer is completely transformed to pernigraniline form current peaks A and C should result in the same area (i.e., in the same Q_A). That effect is especially pronounced in cyclic voltammograms obtained for thicker layers (Fig. 3). The decrease of the current peak C indicates that emeraldine/pernigraniline transformation of POEA layer has not been completed. Pernigraniline is a more rigid form of POEA compared to the emeraldine one. Therefore, due to steric effects caused by ethoxy-group in POEA, pernigraniline form is not energetically favourable. In the case of thicker layers the hindrance is more pronounced, and the transformation to pernigraniline state is of an even lower degree. Mattoso and co-workers [7] explained the observed third current peak decrease (peak C) by the polymer crosslinking, which may be responsible also for the decrease in electroactivity. According to Mattoso et al. that crosslinking might occur in less controllable situations, like higher monomer concentrations or higher potentials. If crosslinking occurs, the same effect and the same conclusion follow, since it is harder to transform polymer to a more rigid pernigraniline form.

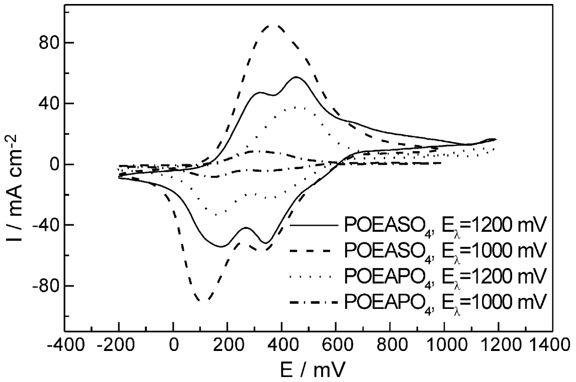

Fig. 3. The voltammograms taken for the 20th cycle of synthesis for POEASO4 and POEAPO4, for different switching potentials.

Fig. 4 illustrates the rates of polymer growth, i.e., the Q_A charge (charge under the current peak A) versus the number of cycles on Pt electrode from two different acid solutions. The growing rate is faster in sulphuric acid solution than in phosphoric acid solution which is in accordance with the results obtained for polyaniline [16]. Wang et al. [23] showed that the synthesis of polyaniline at the beginning is faster in phosphoric acid solution than in sulphuric acid solution, but at a later stage it changes to a faster synthesis in sulphuric acid solution. The higher growing rate in sulphuric acid solution was obtained at a lower switching potential. It is well known that polymer/dimer distribution depends on monomer/radical cation ratio [24]. The experimental conditions leading to the lower monomer/radical cation ratio will favour a dimerisation reaction. At higher potentials the higher amount of radical cation is produced, and thus a lower monomer/radical cation ratio results, i.e., a higher degree

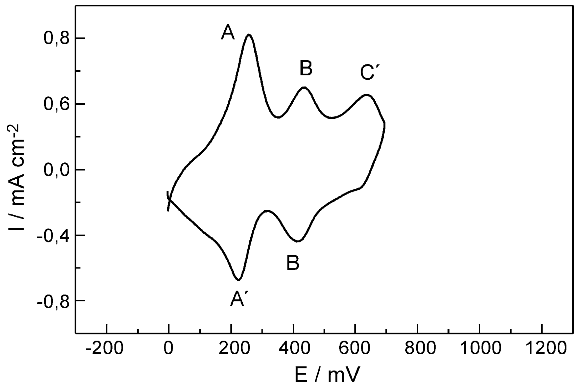

Fig. 2. The voltammogram taken for POEASO4, obtained in Fig. 1(a), in $1\,\mathrm{mol\,dm^{-3}}$ H_2SO_4, $\nu = 2\,\mathrm{mV\,s^{-1}}$.

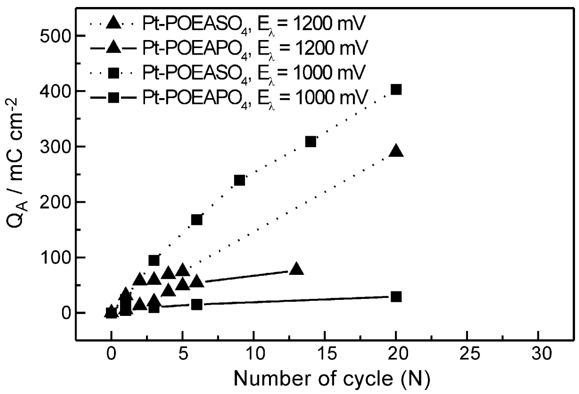

Fig. 4. Charge under the peak A, Q_A, vs. number of cycles (N) during the electrodeposition of POEA in sulphuric and phosphoric acid solutions.

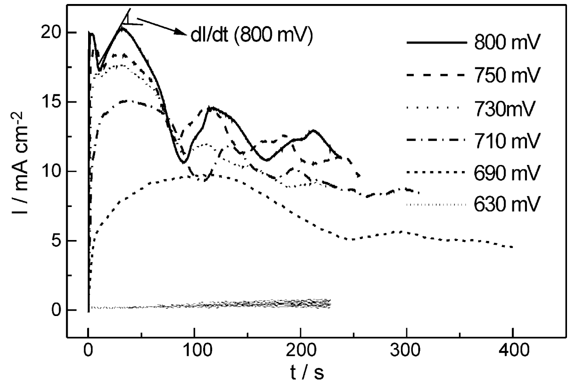

Fig. 5. Current–time transients for the electro-oxidation of *ortho*-ethoxyaniline on Pt at different potentials; $c_{OEA} = 0.5\ \mathrm{mol\ dm^{-3}}$ in $c_{el} = 1.5\ \mathrm{mol\ dm^{-3}}$ H_2SO_4.

of dimerisation, and a smaller amount of polymer, is obtained. The redox reaction of dimer is represented by current peak B [24], and from Fig. 3 it is evident that polymerisation at higher potential results in higher peak B, which is the consequence of an increased formation of radical cations. In phosphoric acid solution, at higher switching potentials, a higher growing rate was obtained. It appears that formation of radical cations in phosphoric acid solution, at higher potentials, is not as high as in sulphuric acid solution. After the initial fast growth, in both acid solutions, the growing rate slows down, and it is not possible to synthesise a layer of POEA as thick as the one in the case of polyaniline [16].

3.2. Nucleation

Figs. 5 and 6 illustrate current–time transients obtained in phosphoric and sulphuric acid solution at different potentials. The characteristic of the transients is a current maximum at short times and a renewed current increase at longer times. In sulphuric acid solution, after the first current maximum, in descending current region a number of maxima appear. The first maximum is followed by a current decrease, and a subsequent sudden current increase, but after a certain time the current decreases again and a new maximum is formed. That phenomenon is qualitatively reproducible. The appearance of a new current maximum might be the consequence of a pealed off polymer layer and a renucleation process on the bare electrode surface (which explains pieces found in the solution of the synthesis). The appearance, the position and the discernibility of current maxima depend on the counter-ion used, and on the applied potential step. The current maximum presents a new phase formation, and a response is similar to that obtained for the metal oxide formation [25]. It can be analysed for the nucleation mechanism by comparing the experimental data with the theoretical plots given for different types of nucleation processes. The theoretical plots for the instantaneous and for the progressive 3D nucleation process under diffusion control are given by Eqs. (1) and (2) [26], respectively:

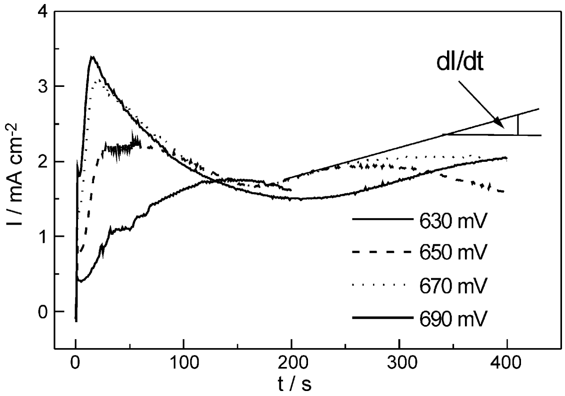

Fig. 6. Current–time transients for the electro-oxidation of *ortho*-ethoxyaniline on Pt at different potentials; $c_{OEA} = 0.5\ \mathrm{mol\ dm^{-3}}$ in $c_{oe} = 3\ \mathrm{mol\ dm^{-3}}$ H_3PO_4.

$$\left(\frac{I}{I_{\mathrm{m}}}\right)^2 = \frac{1.9542}{t/t_{\mathrm{m}}}\left(1-\exp\left(-1.2564\left(\frac{t}{t_{\mathrm{m}}}\right)\right)\right)^2 \tag{1}$$

$$\left(\frac{I}{I_{\mathrm{m}}}\right)^2 = \frac{1.2254}{t/t_{\mathrm{m}}}\left(1-\exp\left(-2.3367\left(\frac{t}{t_{\mathrm{m}}}\right)^2\right)\right)^2 \tag{2}$$

where I is current density at time t, and I_{m} and t_{m} are characteristics of current maximum. Figs. 7 and 8 compare the non-dimensional plots of the experimental results with theoretical plots for instantaneous and for progressive 3D nucleation under diffusion control. It is evident that in phosphoric acid solu-

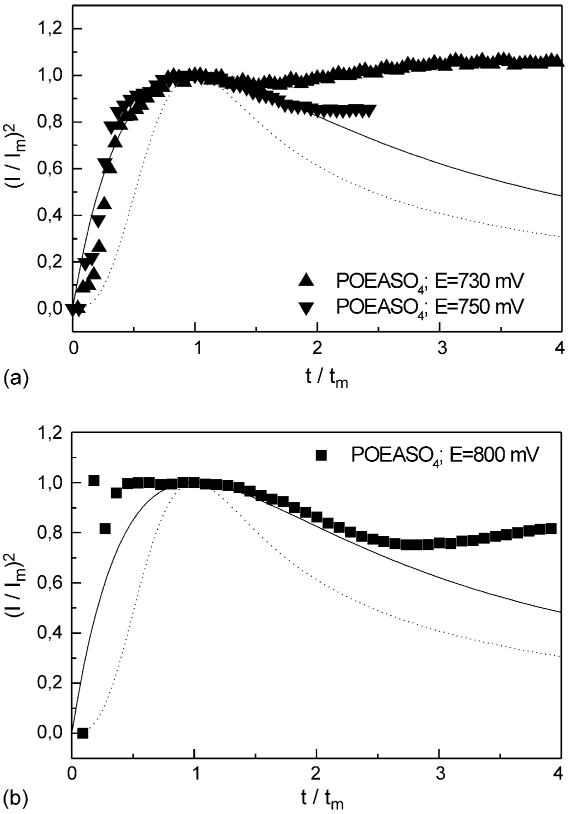

Fig. 7. (a) Non-dimensional plot of current maximum shown in Fig. 5 compared with theoretical curves for instantaneous (solid line) and progressive (dotted line) 3D nucleation under diffusion control. (b) Non-dimensional plot of current maximum shown in Fig. 5 at 800 mV compared with theoretical curves for instantaneous (solid line) and progressive (dotted line) 3D nucleation under diffusion control.

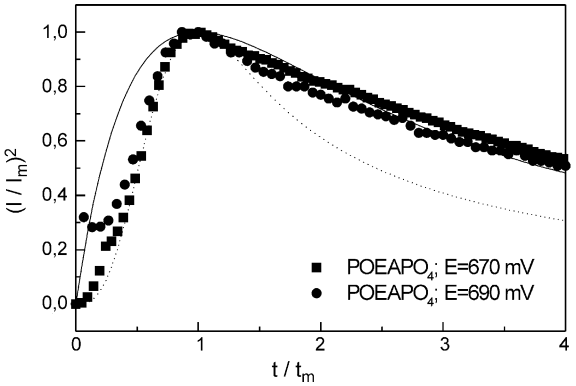

Fig. 8. Non-dimensional plot of current maximum shown in Fig. 6 compared with theoretical curves for instantaneous (solid line) and progressive (dotted line) 3D nucleation under diffusion control.

Table 1
Analysis of current maxima for deposition of POEASO$_4$

E (mV)	$I_m \times 10^3$ (A cm^{-2})	t_m (s)	$I_m^2 t_m$ (A^2 cm^{-4} s)	$N_0 \times 10^{-4}$ (cm^{-2})
730	17.20	7.9	2.34×10^{-3}	2.5
750	19.06	6.5	2.36×10^{-3}	3.0
800	19.91	3.8	1.51×10^{-3}	5.2

tion polymer nucleation follows closely the response predicted for 3D progressive nucleation, and in sulphuric acid solution it follows closely the response predicted for 3D instantaneous nucleation. There is a fairly good agreement between the theoretical and the experimental plots, except for the values which follow the first current maximum. This is explained by the fact that in sulphuric acid solution the current peak is followed by a fast current increase, and the typical current decrease at longer time is not obtained, while in phosphoric acid solution at longer time progressive nucleation changes to the instantaneous one.

From Tables 1 and 2, it is evident that the value $I_m^2 t_m$ is constant, irrespective of the overvoltage applied, which is the criterion for 3D nucleation under diffusion control [26].

In the case of POEA, it is possible that the formation of a compact layer proceeds before the beginning of 3D nucleation process which is under diffusion control, and the evidence for this in sulphuric acid solution is the additional peak, or the shoulder, that is registered at the potential of 800 mV (Fig. 7(b)). At lower potentials this peak is hardly noticeable. The existence of the additional peak at 800 mV can cause a deviation of $I_m^2 t_m$ value. A similar result was obtained in the previous paper [27], where polyaniline nucleation processes were studied, i.e., 3D instantaneous nucleation was obtained in case of higher aniline concentrations and 3D progressive nucleation was obtained in case of lower aniline concentration in 1 mol dm^{-3} HClO$_4$. In that paper, it was shown that there are two separate nucleation processes. The first process might obey kinetic control, and in that stage a compact layer is obtained. After the first stage a new nucleation process appears under different circumstances, and it is shown that the process is under diffusion control.

Table 2
Analysis of current maxima for deposition of POEAPO$_4$

E (mV)	$I_m \times 10^3$ (A cm^{-2})	t_m (s)	$I_m^2 t_m$ (A^2 cm^{-4} s)	$N_s \times 10^{-4}$ (cm^{-2})
670	3.07	21.6	2.04×10^{-4}	28.8
690	3.39	15.8	1.82×10^{-4}	39.4

Cordova et al. [28] obtained 3D progressive nucleation under diffusion control for 0.5 mol dm^{-3} aniline in 0.5 mol dm^{-3} H_2SO_4. In our experiment with the same concentration of monomer, but with *ortho*-ethoxyaniline, in 1.5 mol dm^{-3} H_2SO_4, 3D instantaneous nucleation was obtained. This shows that there are different parameters that influence the nucleation process, like acid concentration, or the type of monomer. Cordova et al. also carried out nucleation of polyaniline in $HClO_4$, under the same circumstances as in H_2SO_4, where the process obeys 3D instantaneous nucleation and 2D progressive nucleation, both occurring almost simultaneously. Bade et al. [29] showed that nucleation from H_2SO_4 at lower aniline concentration proceeds through 2D growth.

For 3D progressive and instantaneous nucleation the diffusion coefficient and the active site number were estimated using equations found elsewhere [25–27]. For *ortho*-ethoxyaniline in sulphuric acid solution, diffusion coefficient, calculated from the current maximum and from the time of the maximum, amounts to $(1.4 \pm 0.1) \times 10^{-6}$ cm^2 s^{-1}. Diffusion coefficient in sulphuric acid solution is similar to the value obtained for aniline in $HClO_4$ ($D = 7.3 \times 10^{-6}$ cm^2 s^{-1}) [27], i.e., within the same order of magnitude. The diffusion coefficient for *ortho*-ethoxyaniline in phosphoric acid solution amounts to 8×10^{-8} cm^2 s^{-1}. The value obtained in phosphoric acid solution is two orders of magnitude smaller than the one obtained for aniline. That can be explained by the fact that monomers must cross high density oligomer region to reach the growing active sites at the electrode surface [28,30]. It is well known that polymer nucleation proceeds through different phases: diffusion of monomers to the electrode surface, oxidation of monomers, diffusion of monomer radical cations towards the solution where oligomerisation takes place, critical size oligomer formation, precipitation to the electrode surface and further growth of precipitated oligomers, i.e., active site growth proceeds until the electrode surface is totally covered [28–30]. Since different diffusion coefficients were obtained, it is fair to conclude that in different acids, different concentrations of oligomers exist close to the electrode surface.

The number of active sites in two different acid solutions is shown in Tables 1 and 2. The number of active sites N_0 is given for the case of instantaneous nucleation (sulphuric acid solution). For the case of progressive nucleation (phosphoric acid solution) the number of active sites at longer times, i.e., after the entire electrode surface is covered by the active sites, N_s is also given. It is evident that in sulphuric acid solution compared to phosphoric acid solution a smaller number of active sites is obtained. Considering that in phosphoric acid solution the nucleation begins as progressive, but after some time changes to the instantaneous, the calculations for the instantaneous nucleation were also carried out. Again, a higher number of active sites was obtained in phosphoric acid solution.

Different nucleation mechanisms are developed in the presence of different anions. Phosphate anions (in this case, dihydrogenphosphate anions) have a higher affinity for the adsorption than sulphate anions (hydrogensulphate anions). Machado and co-workers [31] obtained on Pt electrode 19% coverage by anions in phosphoric acid solution, and 7% in sulphuric acid solution. Since dissociation of H_3PO_4 is low (the first dissociation constant: $pK_a = 2.16$) only a low amount of $H_2PO_4^-$ exists in the solution, so a low amount of $H_2PO_4^-$ on the electrode surface could be expected. But it was shown [32,33] that pK_a value of the adsorbed species decrease significantly compared to pK_a value in the solution. These facts suggest that in phosphoric acid solution anions, and not a non-dissociated form of acid are adsorbed on the electrode surface. The higher coverage with anions promotes coadsorption of *ortho*-ethoxyaniline on the electrode surface before the nucleation process starts. Thus, at the beginning a higher amount of monomers is present on the electrode surface in phosphoric acid solution, as well as a higher amount of oligomers will be formed close to the electrode surface. They are slowly deposited on the electrode surface, inducing a higher oligomer density in the vicinity of the electrode.

A further growth, i.e., the renewed current increase, was interpreted in literature [27,29] as 1D growth of polymer chains with continuous chains branching. From dI/dt slope in Figs. 5 and 6. It follows that a further growth, after the nucleation process, is faster in sulphuric acid solution. The current increase is not exponential as in the case of polyaniline [27,29], indicating that branching of POEA is not pronounced. Consequently, lower molar mass is expected.

4. Conclusions

The results obtained in this work show that electrochemical synthesis of POEA is influenced by anions present in the solution. The obtained polymer has a similar behaviour to the one reported for polyaniline, i.e., it has the same oxidation states but there are differences in the position of current peaks due to the electronic and steric effects of ethoxy-group. In the case of $POEASO_4$, it is possible to resolve a relatively stable state that exists between emeraldine and leucoemeraldine oxidation state.

Polymerisation rate is faster in sulphuric acid solution, compared to phosphoric acid solution, but a different rate trend was obtained at a higher switching potential value. For example, in the case of $POEASO_4$, the synthesis rate slows down while in the case of $POEAPO_4$, with a potential increase, a higher synthesis rate was obtained. Evidently, there is a different monomer/radical cation ratio in different acid solutions and thus different polymer/dimer ratio results.

According to the results obtained, the effect of anions on nucleation process is also evident. Anions present on the electrode surface influence the amount of monomers on the electrode surface as well as the amount of oligomers close to the electrode surface. Thus, different nucleation mechanisms are obtained in sulphuric and phosphoric acid solutions. It is found that nucleation of POEA in sulphuric acid solution proceeds through 3D instantaneous nucleation under diffusion control, and in phosphoric acid solution through 3D progressive nucleation under diffusion control. After the nucleation is completed, the further layer growth under potentiostatic conditions is faster in sulphuric acid solution. Since different nucleation mechanism and different rates of polymer layer growth were obtained, different properties of the layer should result.

Acknowledgement

The financial support from the Ministry of Science of the Republic of Croatia under the 0125-010 grant is gratefully acknowledged.

References

[1] W.A. Gazotti, M.J.D.M. Jannini, S.I. Cordoba de Torresi, M.A. De Paoli, J. Electroanal. Chem. 440 (1997) 193.
[2] C.F.O. Graeff, R.K. Onmori, F.E.G. Guimarães, R.M. Faria, Synth. Met. 105 (1999) 151.
[3] V. Brusic, M. Angelopoulos, T. Graham, J. Electrochem. Soc. 144 (1997) 436.
[4] P.A. Kilmartin, L. Trier, G.A. Wright, Synth. Met. 131 (2002) 99.
[5] J. Widera, M. Skompska, K. Jackowska, Electrochim. Acta 46 (2001) 4125.
[6] S.V. Mello, L.H.C. Mattoso, J.R. Santos Jr., D. Gonçavales, R.M. Faria, O.N. Oliveira Jr., Electrochim. Acta 40 (1995) 1851.
[7] D. Gonçavales, L.H.C. Mattoso, L.O.S. Bulhoes, Electrochim. Acta 39 (1994) 2271.
[8] S. Patil, M.A. More, P.P. Patil, J. Appl. Polym. Sci. 74 (1999) 3009.
[9] M. Mazur, P. Krysinski, Electrochem. Acta 46 (2001) 3963.
[10] Lj. Duić, Z. Mandić, F. Kovačiček, J. Polym. Sci. Part A Polym. Chem. 32 (1994) 105.
[11] J. Widera, B. Palys, J. Bukowska, K. Jackowska, Synth. Met. 94 (1998) 265.
[12] L.H.C. Mattoso, S.K. Manohar, A.G. MacDiarmid, A.J. Epstein, J. Polym. Sci. Part A Polym. Chem. 33 (1995) 1227.
[13] M. Leclerc, G. D'Aprano, G. Zotti, Synth. Met. 55–57 (1993) 1527.
[14] A. Raghunathan, P.K. Kahol, B.J. McCormick, Synth. Met. 100 (1999) 205.
[15] J.P. Pouget, S.L. Zhao, Z.H. Wang, Z. Oblakowski, A.J. Epstein, S.K. Manohar, J.M. Wiesinger, A.G. Macdiarmid, C.H. Hsu, Synth. Met. 55–57 (1993) 341.
[16] M. Kraljić, Z. Mandić, Lj. Duić, Corros. Sci. 45 (2003) 181.
[17] M.C. Bernard, S. Joiret, A. Hugot-Le Goff, P.V. Phong, J. Electrochem. Soc. 148 (2001) B12.
[18] S.R. Moraes, D. Huerta-Vilca, A.J. Motheo, Prog. Org. Coat. 48 (2003) 28.
[19] Lj. Duić, Z. Mandić, J. Electroanal. Chem. 335 (1992) 207.
[20] Y.B. Shim, S.-M. Park, Synth. Met. 29 (1989) E169.
[21] Lj. Duić, M. Kraljić, S. Grigić, J. Polym. Sci. Part A Polym. Chem. 42 (2004) 1599.
[22] Lj. Duić, S. Grigić, Polimeri 18 (1997) 176.
[23] B. Wang, J. Tang, F. Wang, Synth. Met. 18 (1987) 323.
[24] Lj. Duć, Z. Mandić, S. Kovač, Electrochim. Acta 40 (1995) 1681.
[25] Z. Grubač, M. Metikoš-Huković, Electrochim. Acta 43 (1998) 3175.
[26] B. Scharifker, G. Hills, Electrochim. Acta 28 (1983) 879.
[27] Z. Mandić, Lj. Duić, F. Kovačiček, Electrochim. Acta 42 (1997) 1389.
[28] R. Córdova, M.A. del Valle, A. Arratia, H. Gómez, R.J. Schrebler, J. Electroanal. Chem. 377 (1994) 75.
[29] K. Bade, V. Tsakova, J.W. Schultze, Electrochim. Acta 37 (1992) 2255.
[30] M.A. del Valle, P. Cury, R. Schrebler, Electrochim. Acta 48 (2002) 397.
[31] M.C. Santos, D.W. Miwa, S.A.S. Machado, Electrochem. Commun. 2 (2000) 692.
[32] G. Horány, E.M. Rizmayer, J. Electroanal. Chem. 93 (1978) 183.
[33] O. Koga, Y. Watanabe, M. Tanizaki, Y. Hori, Electrochim. Acta 46 (2001) 3083.