Electrochemical copolymerisation of luminol with aniline: A new route for the preparation of self-doped polyanilines

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Abstract

Electrochemical copolymerisation of luminol and aniline from acidic aqueous medium onto gold electrodes has been investigated. Cyclic voltammetry in combination with electrochemical quartz crystal microbalance (EQCM) have been used to study both the *in situ* growth and redox switching process. In monomer free solution, the deposited polymers are stable and electrochemically active but distinct behaviour is shown by poly(luminol-aniline) films obtained from solutions with different monomers concentration ratio. In acidic medium, the current–voltage profiles range from a polyluminol (one pair of redox couple) to a polyaniline like redox conversion (three redox couples) as the aniline concentration increases. Unlike polyaniline, all prepared copolymers display well expressed electroactivity in sodium carbonate medium (pH 8), which also extends with the aniline content. The self-doping role assured by luminol moiety in the copolymer is also retrieved from the simultaneously recorded EQCM data.

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1. Introduction

Polyaniline (PAni) is one of the most studied conducting polymers [1–3].

PAni films become electrochemically inactive at pH above 4 which limits its use to acidic media. In the last decade, the search of self-doped polyanilines enabling the extension of its electroactivity to neutral and alkaline aqueous solutions has received particular attention. Self-doping can be achieved by sulphonation of polyaniline with fuming sulphuric acid treatment [4], doping of the polyaniline with organic acids such as camphorsulphonic acid (CSA) [5] or by polymerisation of aniline derivatives bearing ionogenic groups such as sulphonic [6–8] or carboxylic acids [6,9] and hydroxyl groups [10]. The

latter approach has been used in electrochemical copolymerisation studies with aniline. In general, the copolymerisation of aniline and its derivatives presents lower polymerisation rates than observed for aniline, depends on the monomers concentration ratio in the polymerisation solution and the substituted anilines difficult the aniline polymerisation [7,10].

Wang and Knoll [9] reported that for the copolymer of aniline and its carboxylated derivative (AA) the separation between the cathodic and anodic peaks (ΔE_{p1} and ΔE_{p2}) observed for the films in acidic media depends on the monomers concentration ratio in the polymerisation solution; for the PAA films smaller ΔE_{p1} than for PAni indicates more reversible process due to the intra-molecular self-doping between the carboxylic groups and amino nitrogen atoms whereas the increase of the ΔE_{p2}, when compared with PAni, is produced by the reduction of the planar π-conjugation which enhances the energy gap between the emeraldine and the fully oxidised forms of the polymer. For the copolymer, with equal molar content of the two monomers in the polymerisation solution, both ΔE_{p1} and ΔE_{p2} values presents a minimum which means that better reversibility of the two redox

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processes can be achieved by the control of the film composition [9].

Together with the improved electrochemical activity of the self-doped copolymers in neutral and alkaline media, several techniques have been used to study the copolymer composition and properties. By XPS analysis, it was found by Tang et al. [7,8] that the copolymer composition, from aniline and aniline-2,5-disulphonic acid, depends on the monomers ratio in the growth solution; for poly(aniline-co-*o*-aminophenol) films, Liu et al. [10] reported from *in situ* FTIR data the presence of hydroxyl-substituted aniline units in a *head-to-tail* copolymer structure similar to polyaniline.

Luminol (3-aminophthalhydrazide) is an aniline derivative [11,12] widely used in luminescence and electrochemiluminescence studies [13–15] that can be electrochemically polymerised.

Although the polymerisation mechanism is not fully understood, it is likely to occur similarly to aniline through a linkage of an –NH$_2$ group with the *para*-carbon atom of another luminol (Lum) molecule [12]. In acidic medium, two oxidation peaks are observed for luminol; at the potential of the first wave, the electropolymerisation of Lum onto gold, platinum and glassy carbon surfaces yielding electroactive and stable polyluminol (PLum) films have been reported [13,16,17]. Electrochemical quartz crystal microbalance, the proved suitable method to investigate both the electropolymerisation and redox behaviour of conducting polymers [10,18–20] has also been used to study the PLum films growth. This technique allowed to observe that the PLum deposition occurs at potential values above 0.75 V (versus SCE) [14,16].

The PLum films display a single redox switching process [13,14,16] with formal potential at about 0.48 V (versus SCE). Their electroactivity and stable behaviour has been observed in a wide range of pH values, with a potential shift of the redox switching process of −58 mV/pH unit between pH 1 and 11 [13,14,16]. The pH response is suggested to be due to the deprotonation of the PLum –CO–NH–NH–CO– group [14].

Presenting an ionogenic functional group (with pK_a of the monomer at about 6.35 and 15.21 [11]), PLum is a suitable polymer to display self-doping properties with improved pH dependent characteristics such as conductivity and electroactivity in alkaline medium. Moreover, the electropolymerisation of Lum with Ani may improve the polymer deposition as it was suggested for the copolymerisation of *o*-aminophenol with Ani [10].

Envisaging a novel self-doped copolymer, the present work aims to investigate the effect of the monomers, Lum and Ani, concentration ratio in the polymerisation solution on the electrosynthesis. Using cyclic voltammetry in combination with electrochemical quartz crystal microbalance (EQCM), the growth and redox behaviour in acidic and alkaline medium of poly(Lum-Ani) films is investigated.

2. Experimental

The electrochemical quartz crystal microbalance experiments have been performed with a frequency analyser (CH Instruments model 420) in a single compartment cell. The working electrode was an 8 MHz AT-cut quartz crystal coated with 1000 Å Au (0.2 cm^2 geometrical area), a Pt wire was used as counter electrode and a saturated calomel electrode (SCE) as reference. For the frequency variations treatment, a rigid layer behaviour of the deposited films has been assumed and thus using the Sauerbrey equation [21] a negative frequency shift of 1 kHz equals an electrode-mass increase of 7 μg.

PLum and P(Lum-Ani) films were potentiodynamically grown on the Au working electrode by cycling the potential at $v = 50$ mV s^{-1} scan rate, between 0 and 0.875 V versus SCE (polyluminol) and 0.95 V versus SCE (poly(luminol-aniline)) in a 0.5 mol dm^{-3} H$_2$SO$_4$ (Fluka, p.a.) solution containing 0.5 mmol dm^{-3} of luminol (Fluka) and aniline (distilled and kept under N$_2$ atmosphere, at 4 °C) with concentrations ranging from 0 to 30 mmol dm^{-3}.

The polymer layers were washed with monomer free solution, H$_2$SO$_4$ 0.1 mol dm^{-3} and characterised electrochemically (by cycling the potential at 50 mV s^{-1}) in H$_2$SO$_4$ 0.1 mol dm^{-3} (pH 1) and 0.1 mol dm^{-3} sodium carbonate solutions (di-sodium carbonate and sodium hydrogen carbonate, Merck, p.a.) (pH 8).

Prior to all measurements the solutions, prepared with Milli-Q water, were degassed with N$_2$ (99.9999%) for 15 min.

The polyluminol and poly(luminol-aniline) films will be referred as PLum and P(Lum-Ani), followed by the monomers concentration ratio (luminol:aniline); since constant luminol concentration (0.5 mmol dm^{-3}) has been used in all experiments, and 0.5, 2, 10, 20 and 30 mmol dm^{-3} aniline concentration in the copolymerisation experiments, P(Lum-Ani) will be designated as (1:1), (1:4), (1:20), (1:40) and (1:60), respectively.

3. Results and discussion

3.1. Potentiodynamic electropolymerisation of luminol and aniline from acidic media

The successful potentiodynamic formation of polyluminol (PLum) films at several electrode materials in strongly acidic aqueous solutions have been reported [12,14,16,17]. The published results are consistent with a polymer deposition as retrieved from the analysis of the cyclic voltammograms and the change in frequency of the EQCM measurements.

Fig. 1 shows the typical responses of the gold electrode, in 0.5 mol dm^{-3} H$_2$SO$_4$ containing 0.5 mmol dm^{-3} luminol, for 10 consecutive potential scans in the 0.0–0.875 V interval. The current at potentials higher than 0.75 V indicates the luminol oxidation and its depression along the multicycle voltammograms suggest the electrode surface screening by the formation of poor conducting product; the corresponding EQCM results confirm that the frequency only changes after the monomer is oxidised and the decrease observed within 0.800–0.875 V support the occurrence of a deposition which slows down with the consecutive potential cycling. From the changes in the resonant frequency of the microbalance, during the luminol electropolymerisation cycles, it was possible to observe that after a significant mass deposition in the first cycle, it increases almost linearly with the subsequent sweep cycles, as shown in the inset
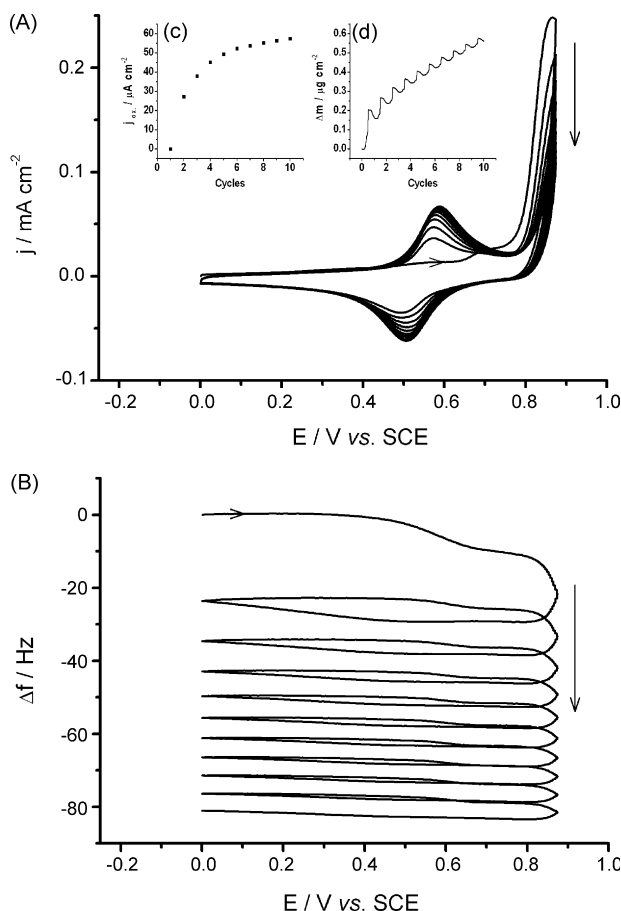
Fig. 1. Consecutive cyclic voltammograms obtained for a gold electrode at a sweep rate of $50\,mV\,s^{-1}$ in $0.5\,mol\,dm^{-3}$ H_2SO_4 + $0.5\,mmol\,dm^{-3}$ luminol (A) and simultaneously recorded EQCM frequency change responses (B). Insets: Evolution of the polymer oxidation peak current density (c) and of the mass change (d) with the polymerisation cycles (10 cycles).

(d) of Fig. 1. In spite of the referred linearity, the current density of the polyluminol oxidation peak, inset (c) of Fig. 1, does not follow the mass changes, tending to a plateau.

The evaluation of the mass increase, using the Sauerbrey equation [22], provided $0.16\,\mu g\,cm^{-2}$ for the first potential scan, $0.30\,\mu g\,cm^{-2}$ for the first three cycles and $0.56\,\mu g\,cm^{-2}$ produced at the end of the experiment (10 cycles).

As can be seen in Fig. 1A, the first reverse potential scan exhibits a reduction peak at 0.50 V with an anodic counterpart revealed in the following anodic sweep at about 0.57 V. Although not monotonically, the respective currents of these pair of peaks increase with the number of cycles and thus they have been attributed to PLum redox conversion [14,16]. These processes appear to take place with a slight increase (reduction) and decrease (oxidation) of mass, as the corresponding changes in frequency reveal (Fig. 1B). It is worthwhile to note that promoting the luminol oxidation at higher potentials, e.g. 1.20 V, an additional pairs of weak peaks at about 0.22 V (reduction) and 0.35 V (oxidation) have been detected and also considered characteristic of the formed polymer of luminol [12].

However, as pointed out by Koval'chuck et al. [23], one would expect that PLum conversion would occur at similar poten-

tial values than those well known for polyaniline (PAni), e.g. oxidations at about 0.20 and 0.80 V. Thus, to explain the above-mentioned current peaks, a more detailed analysis is required and has been carried out.

Due to the limit of solubility, the electrochemical oxidation of luminol in aqueous acidic media has been studied in solutions containing monomer concentrations lower than $1\,mmol\,dm^{-3}$. In what concerns the electrochemical synthe-
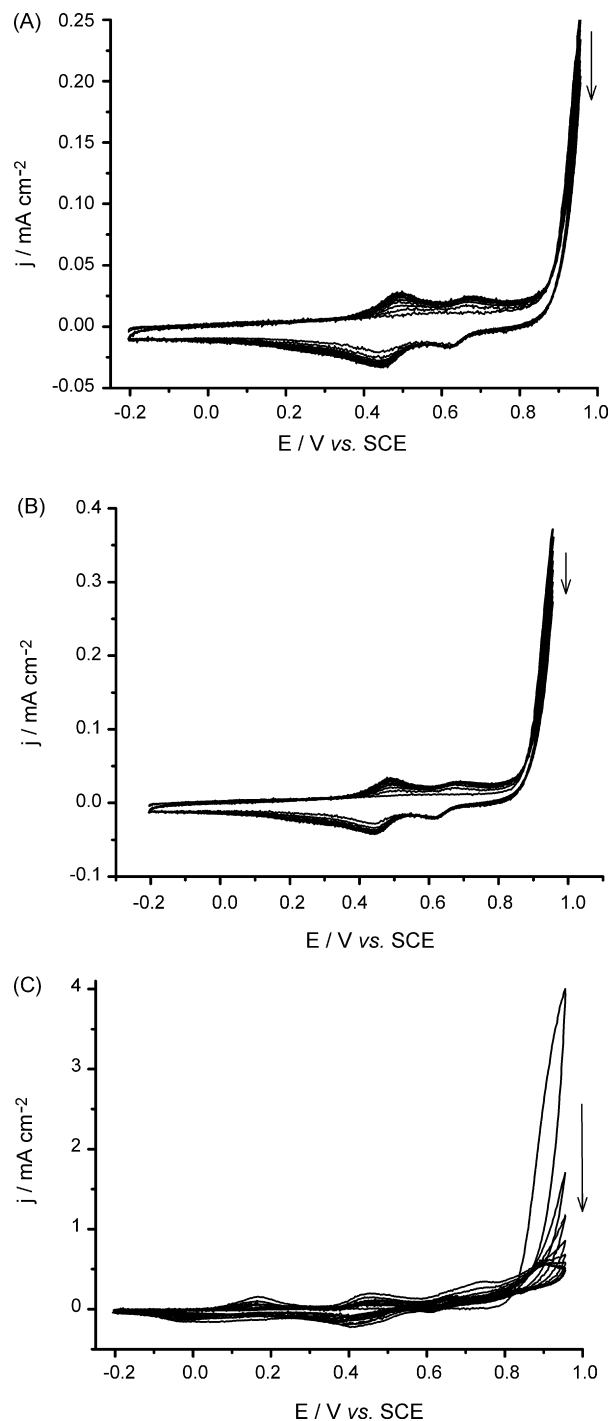

Fig. 2. Consecutive cyclic voltammograms obtained for a gold electrode at a sweep rate of $50\,mV\,s^{-1}$ in $0.5\,mol\,dm^{-3}$ H_2SO_4 + $1\,mmol\,dm^{-3}$ aniline (A), $2\,mmol\,dm^{-3}$ aniline (B) and $30\,mmol\,dm^{-3}$ aniline (C).

sis of PAni, a general reaction scheme involving a dimer, the 4-aminodiphenylamine (ADPA), as an intermediate in the polymer growth, has been accepted, on the basis of earlier studies [24,25]. On the other hand, a number of papers devoted to the study of PAni and to the understanding of the change in the film behaviour in dependence of electrosynthesis experimental parameters, provide evidence on the important role of the monomer concentration in the preparation solution, in the resulting polymer–dimer distribution [26] and over the oxidation–reduction properties of the obtained PAni films [26–28].

Fig. 2 contrasts the repetitive cyclic voltammograms of the gold electrode in $0.5 \, mol \, dm^{-3}$ H_2SO_4 containing different concentrations of aniline (1, 2 and $30 \, mmol \, dm^{-3}$) using the same experimental parameters as described for luminol, except the anodic potential limit which has been extended to $0.95 \, V$ to attain the aniline oxidation in the present experimental conditions.

For low monomer concentrations (Fig. 2A and B), only current peaks ($E = 0.49 \, V$) generally assumed as representing dimer and dimer hydrolysis products [26,29,30] are detected;

the typical leucoemeraldine/emeraldine (E about $0.17 \, V$) and emeraldine/pernigradiline (E about $0.74 \, V$) conversions, can only be clearly noticed by increasing the aniline concentration (Fig. 2C).

The general similarities among the results displayed in Figs. 1 and 2A and B, allow to conclude that in aqueous media, due to the very low concentration of luminol that can be used, the rapid increase in the radical cation/monomer ratio, after luminol oxidation will prevail the formation of a dimer as a result of the coupling of two radical cations. By analogy with that reported for the anodic oxidation of aniline, this product can also polymerise but resulting in an oligomeric form, very likely an octamer [26,31,32].

It must be noted that the peak current reflecting the oxidation of the final deposited product is lower for the case of aniline than recorded for the experiments with luminol (Fig. 1) likely due to a more sluggish pathway in the former case.

Luminol contains an aromatic amino-group that should enable to co-polymerise with aniline. This co-polymerisation of luminol and aniline has been attempted and Fig. 3 illustrates the
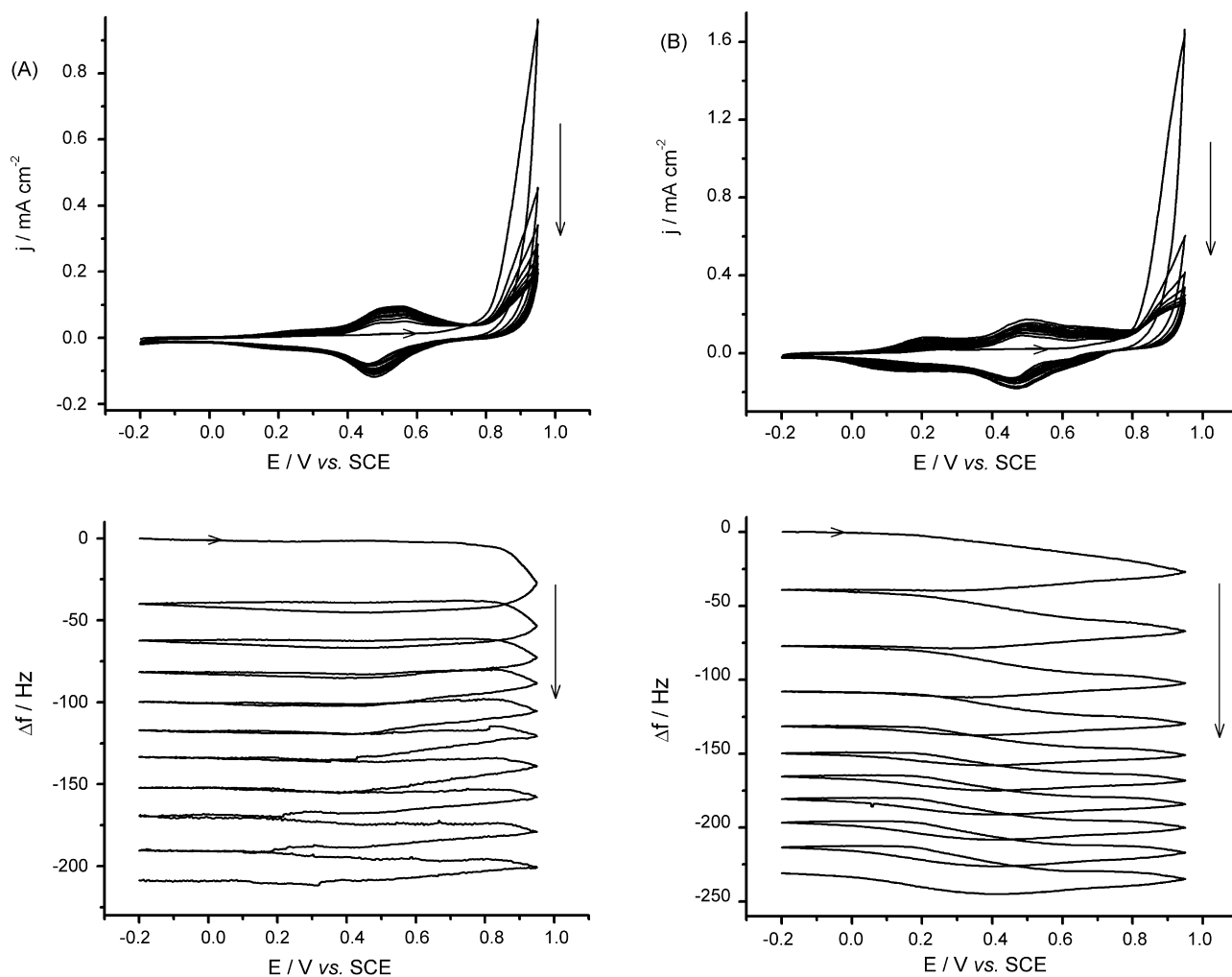

Fig. 3. Consecutive cyclic voltammograms and simultaneously recorded EQCM frequency change responses, obtained for a gold electrode at a sweep rate of $50 \, mV \, s^{-1}$ in $0.5 \, mol \, dm^{-3}$ H_2SO_4 + constant concentration of luminol ($0.5 \, mmol \, dm^{-3}$) and $10 \, mmol \, dm^{-3}$ aniline (A), $20 \, mmol \, dm^{-3}$ aniline (B) and $30 \, mmol \, dm^{-3}$ aniline (C).
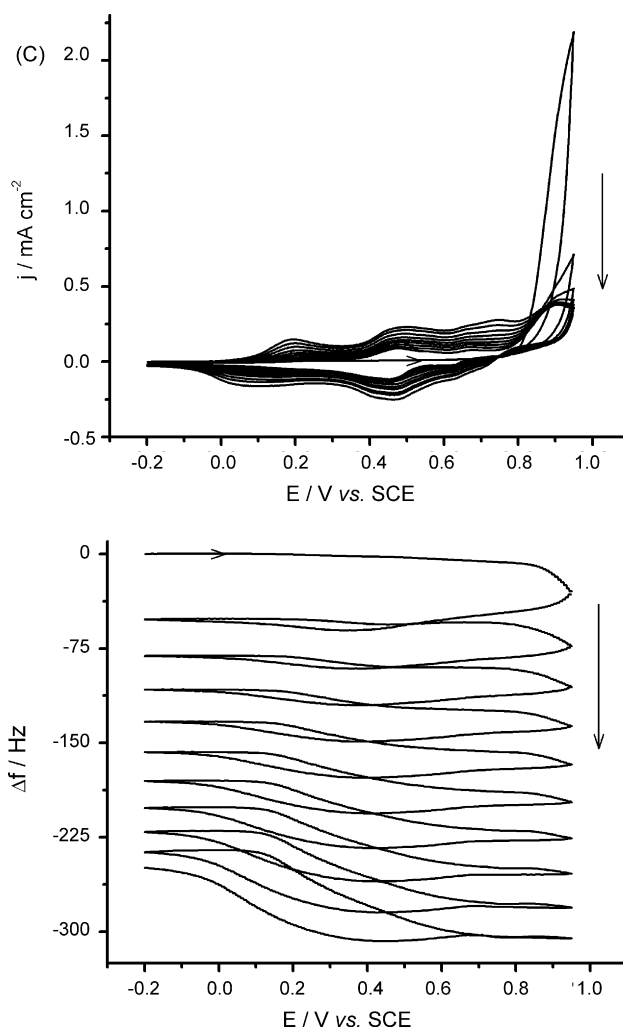
Fig. 3. (*Continued*).

influence of aniline concentration (10, 20 and 30 mmol dm^{-3}) on the development of the deposited products for the same concentration of luminol (0.5 mmol dm^{-3}). From 1:20 luminol:aniline molar ratio (Fig. 3A), it is mainly formed by the above mentioned oligomer, as revealed by the prominence of the redox processes at about $E = 0.53$ V and almost featureless change in frequency during the subsequent potential scans. By increasing the aniline concentration to 20 mmol dm^{-3} (Fig. 3B), the wave for leucoemeraldine/emeraldine transformation appear, increases with the number of cycles and after the fifth cycle originates, although slight, the expected change in frequency; besides the apparent merging of the anodic peaks previously observed at about 0.50 V,

the respective final current value is identical to that recorded in Fig. 3A; finally, at about $E = 0.70$ V it is weakly noticeable another process.

The comparison of the deposited mass obtained for each P(Lum-Ani) film after 10 potential cycles (Table 1) indicates that the presence of aniline in the polymerisation solution facilitates the polymer growth, likely due to an easier charge transfer at the electrode surface with the insertion of Ani units on the polymer structure [10].

The fact that the increase in aniline concentration favours the first peak, indicating the leucoemeraldine/emeraldine conversion, and has no significant effect on the middle pair of peaks, as shown by the results in Fig. 3C, suggest the development of a new polymer phase, with interspersed products of the oxidation of luminol (short segments) in a PAni skeleton.

3.2. Copolymers redox behaviour

The voltammetric behaviour of PLum, PAni and P(Lum-Ani) films was investigated in 0.1 mol dm^{-3} H$_2$SO$_4$. Figs. 4 and 5 depict the simultaneously obtained frequency shifts and current responses of the PLum and P(Lum-Ani) modified QC elec-
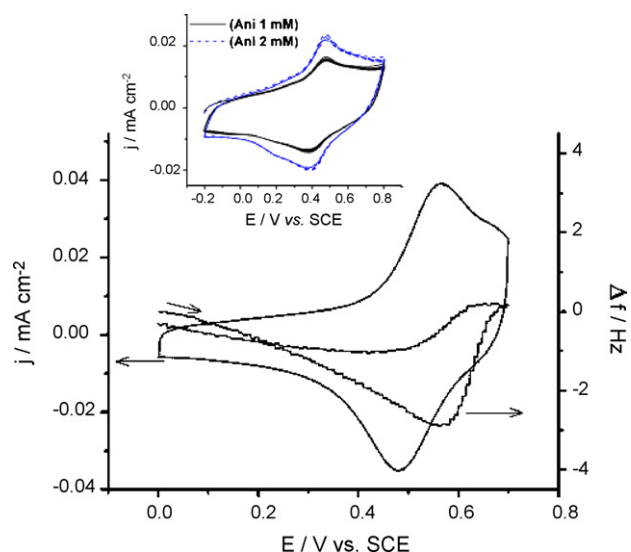
Table 1
P(Lum-Ani) mass deposited after potentiodynamic polymerisation (10 cycles from 0.0 to 0.95 V; $\nu = 50$ mV s^{-1})

Film	m/μg cm^{-2}
P(Lum-Ani) (1:1)	1.07
P(Lum-Ani) (1:4)	1.10
P(Lum-Ani) (1:20)	1.42
P(Lum-Ani) (1:40)	1.60
P(Lum-Ani) (1:60)	1.72

Fig. 4. Cyclic voltammograms and simultaneously recorded responses of Δf during PLum redox conversion in 0.1 mol dm^{-3} H$_2$SO$_4$. The inset shows the redox behaviour of PAni prepared from low concentrated solutions.

trode, respectively. Reproducible signals were obtained after a few number of consecutive potential cycles; no significant "first cycle effect" was observed for PLum (or for PAni prepared from low concentration solution, as illustrated in the inset of Fig. 4).
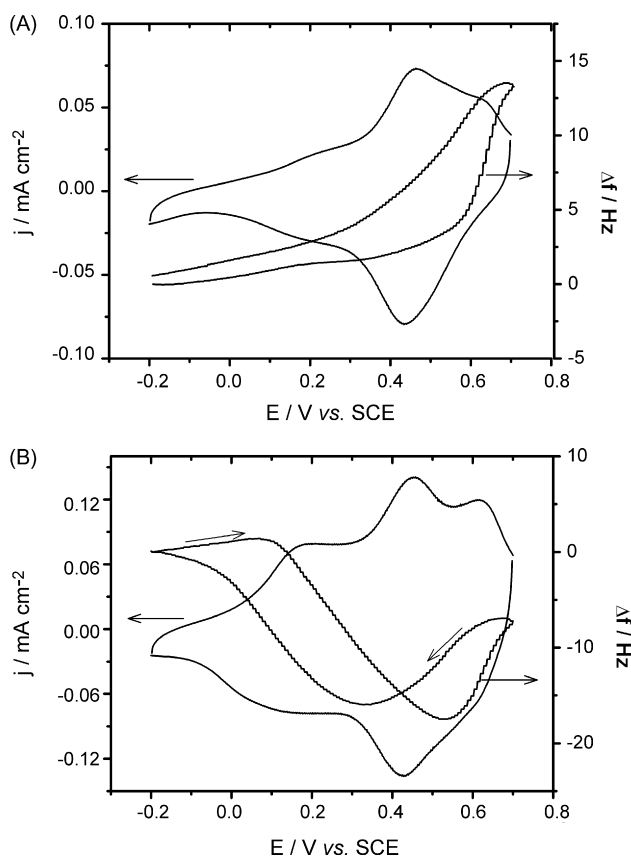
There is a well developed pair of current peaks in the cyclic voltammetric curve for PLum, and the polymer oxidation and reduction involves about the same charge. The oxidation starts at about 0.45 V, with a current maximum at 0.56 V followed by an ill-defined shoulder; the cathodic peak occurs at $E = 0.48$ V. The frequency decreases slowly when the potential is scanned from 0.0 to 0.55 V and increases fast thereafter up to the end of the anodic scan, reaching its original value. Due to the acidic nature of the solution, the polymer might be slowly protonated and the charge compensation implies the ingress of anions being both rapidly expulsed upon polymer oxidation. The relatively small increase in mass observed when the potential is swept from 0.60 to 0.50 V might be due to fast protonation followed by slow egress of solvent.

For the P(Lum-Ani) prepared from solutions, containing the monomers in 1:20 ratio (Fig. 5A), the initial change in the frequency reflects the presence of leucoemeraldine and its oxidation to emeraldine, with a slight decrease in mass. The redox conversion denoted by the middle current peak appears reversible and the subsequent oxidation process is better defined; therefore, in this potential region, the doping/dedoping process, may involve the same type of egress/ingress of solution species than observed for PLum, but occurs much faster, and so the frequency signal returns to close to its initial value when the potential cycle is complete.
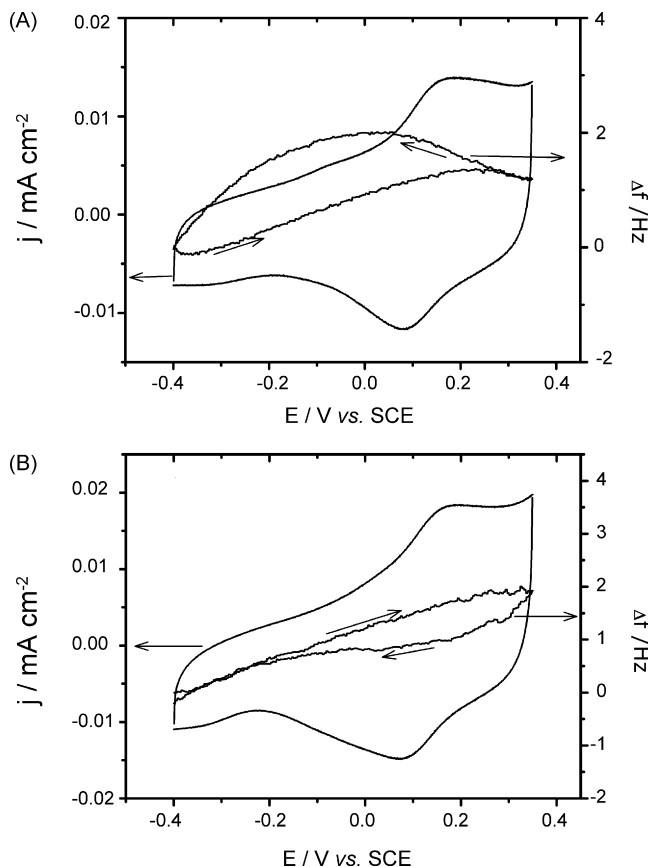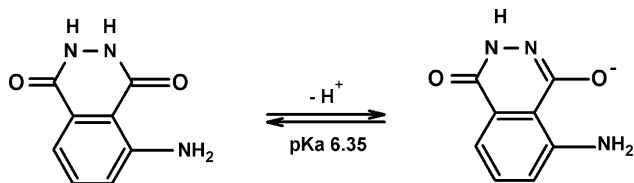

Fig. 5. Cyclic voltammograms and simultaneously recorded responses of Δf during P(Lum-Ani) redox conversion in 0.1 mol dm^{-3} H$_2$SO$_4$. Films prepared from 0.5 mol dm^{-3} H$_2$SO$_4$ + constant concentration of luminol (0.5 mmol dm^{-3}) and 10 mmol dm^{-3} aniline (A) and 20 mmol dm^{-3} aniline (B).

Fig. 6. Cyclic voltammograms and simultaneously recorded responses of Δf during PLum (A) and P(Lum-Ani) (B) redox conversion in 0.1 mol dm^{-3} carbonate solution (pH 8). P(Lum-Ani) prepared from 0.5 mol dm^{-3} H$_2$SO$_4$ + 0.5 mmol dm^{-3} luminol and 0.5 mmol dm^{-3} aniline.

Scheme 1.

Different trends are found in the current response but particularly in the frequency signal during the oxidation and reduction of P(Lum-Ani) films obtained from solutions with 1:40 monomers ratio (Fig. 5B). In the voltammograms, the middle current peak is still predominant but the peaks representing leucoemeraldine/emeraldine and emeraldine/pernigraniline transformations are defined; the frequency decrease when the potential is scanned from −0.20 to 0.50 V and increase from 0.50 to 0.70 V during the positive scan, as well as the changes observed in the negative potential sweep, are qualitatively similar to the reported for PAni films [26,29]. However, the large frequency change in both scan directions, for $E > 0.40$ V (after the middle pair of peaks) and the observed hysteresis in this potential region is not typical for PAni but already reported for co-polymer with aniline [10].

The electrochemical inactivity of PAni in alkaline media has been widely reported [33–35]. Being luminol a derivative of aniline and t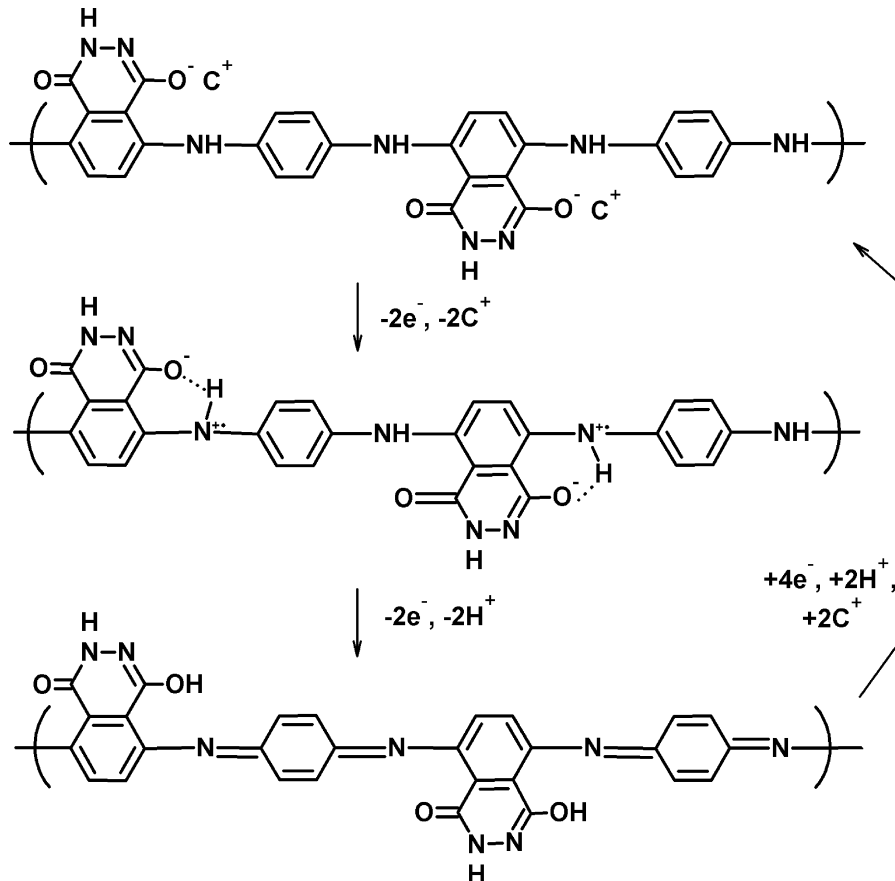he polymerisation process similar to the parent monomer, PLum is also expected to be electroinactive at high pH [12]. Notwithstanding, a redox response of PLum film, synthesised on a glassy carbon electrode, in the pH range of 1–11 has been observed [14] and attributed to the deprotonation of the –CO–NH–NH–CO– group.

The cyclic voltammograms and frequency variation simultaneously recorded during the characterisation of the PLum and P(Lum-Ani) films in alkaline 0.1 mol dm^{-3} carbonate solution (pH 8) are represented in Figs. 6–8.

As previously reported [17], PLum and P(Lum-Ani) films are electroactive in alkaline medium. Reversible redox behaviour is observed for both PLum (Fig. 6A) and P(Lum-Ani) films, either prepared from solutions with very low monomer concentration (Fig. 6B) or when the Ani content has been increased (Figs. 7 and 8). The doping/dedoping process is revealed by a single pair of peaks that, as expected, occurs at more negative potential values than observed in acid media; by increasing the Ani concentration in the polymerisation solution, there is a peak potential shift towards the cathodic path.

In this medium, Lum is deprotonated at the hydrazine group yielding an anion [15] as illustrated by Scheme 1. The deprotonated hydrazine group can undergo oxidation in alkaline medium (step involved in the electrochemiluminescence emission of Lum).

The presence of anionogenic groups in the PLum and P(Lum-Ani) films structure allow to consider that the redox switching
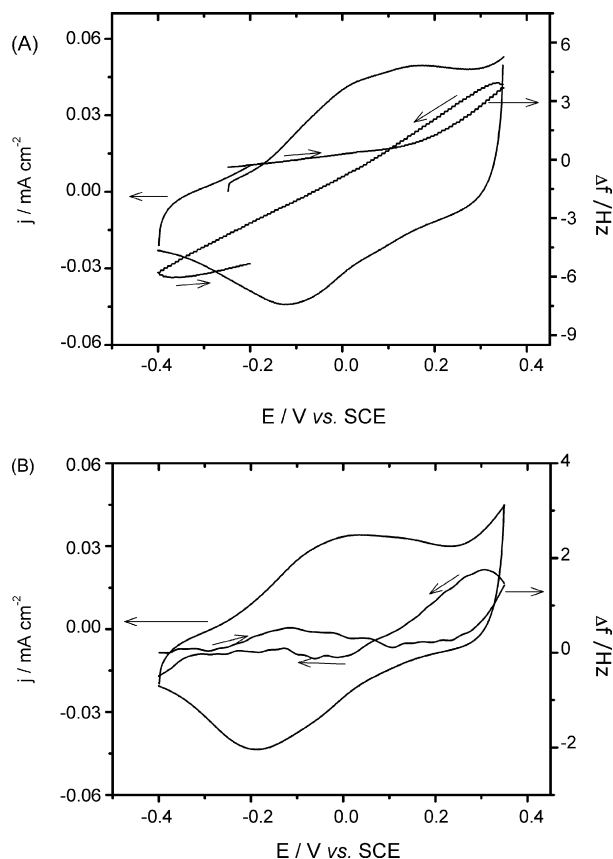

Scheme 2.

Fig. 7. Cyclic voltammograms and simultaneously recorded responses of Δf during P(Lum-Ani) redox conversion in 0.1 mol dm^{-3} carbonate solution (pH 8). Films prepared from 0.5 mol dm^{-3} H$_2$SO$_4$ + 0.5 mmol dm^{-3} luminol and 10 mmol dm^{-3} aniline. First cycle after holding the potential at reduction potential for 5 min (A) and after more than 10 multicycles potential scans (B).

of these copolymers proceeds through a mechanism similar to self-doped polyanilines derivatives, being the charge compensation mainly at the expense of cations (protons and sodium ions) into or from the polymer [36,37]. Accordingly, in Scheme 2 a plausible pathway for the redox switching process of PLum and P(Lum-Ani) films is presented.

The presence of negatively charged groups within the polymer structure, as the deprotonated hydrazine group of Lum, enable the stabilisation and charge compensation of the positively charged nitrogen atom, formed upon oxidation, and anions are not required to ingress the film for charge compensation. The lower frequency changes observed for the PLum and P(Lum-Ani) upon oxidation in pH 8 solution, when compared with the variations obtained in acidic medium, support the pathway given in Scheme 2.

The formation of a stable six-member ring, as reported for sulphonic acid ring-substituted polyaniline, SPAn [38], when the copolymers are in alkaline media is an hypothesis deserving further investigation.

The memory effect of the co-polymers of aniline with luminol has also been analysed and Fig. 7 shows the cyclic voltammograms and changes in the frequency obtained in the first potential scan after holding the modified electrode at cathodic potential for 5 min (Fig. 7A) and under multicycle conditions (Fig. 7B). The anodic current peak observed in the first scan is a bit higher while the redox conversion occurs at more negative values under repetitive cycling. The observed changes are much less expressed than those reported for polyaniline [39] where the anion movement during redox cycling of the polymer is often considered the responsible for the slow relaxation behaviour. In the present case, self-doping co-polymers, this
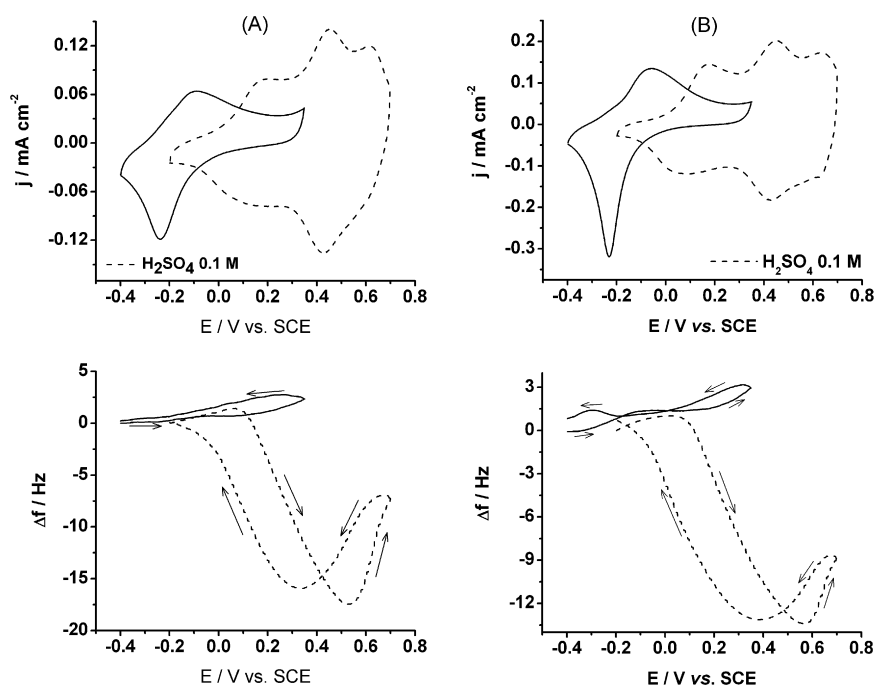

Fig. 8. Cyclic voltammograms and simultaneously recorded responses of Δf during P(Lum-Ani) redox conversion in 0.1 mol dm^{-3} carbonate solution (pH 8). Films prepared from 0.5 mol dm^{-3} H$_2$SO$_4$ + constant concentration of luminol (0.5 mmol dm^{-3}) and 20 mmol dm^{-3} aniline (A) and 30 mmol dm^{-3} aniline (B). For comparison, the data obtained in acid media (0.1 mol dm^{-3} H$_2$SO$_4$) are also shown.

explanation is precluded since the charge compensation during the redox switching is assured by cation transport. The decrease in height of the anodic peak and the shift to negative direction on the potential scale of both anodic and cathodic waves suggest a gradual structural organisation of the polymer chains and/or a slow decomposition of the copolymer.

The behaviour in pH 8 media of the co-polymers prepared from solutions with high content in aniline (1:40 and 1:60) (Fig. 8) display a remarkable similarity with copoly(aniline-2aminonaphthalene-4,8-disulphonic acid) in pH 7 solution [37]: a clear anodic peak and a corresponding sharp cathodic peak are observed; the oxidation and reduction processes of P(Lum-Ani) are also centred at around a favourable value (-0.10 V) if active electrode materials are envisaged. Consistent with a doping process assured only by protons movement, no change in mass occurs.

4. Conclusions

The electropolymerisation of luminol and aniline with luminol were investigated using combined cyclic voltammetry and EQCM technique. It was found that although the nature of the deposited product is dependent on the molar ratio of the monomers in the polymerisation solution, a copolymerisation occurs. The growth of the copolymers initially proceeds near linearly with increasing number of potential cycles, but the polymerisation speed tends to decrease and thin films are created.

In acidic solution, the copolymers electrochemical properties are similar to those of the parent polyaniline. The results show that the copolymerisation extends the films electroactivity in solutions with pH 8. This behaviour is attributed to a self-doping effect due to the presence in the film of negatively charged sites resulting from the deprotonation of the hydrazine group of luminol in alkaline media. In agreement is the featureless frequency response of the copolymer modified QC electrode along the well-defined redox switching observed in sodium carbonate solution.

Acknowledgement

References

[1] J. Heinze, Synth. Met. 41–43 (1991) 2805.
[2] G. Inzelt, M. Pineri, J.W. Schultze, M.A. Vorotyntsev, Electrochim. Acta 45 (2000) 2403.
[3] D. Zhang, Y. Wang, Mater. Sci. Eng. B 134 (2006) 9.
[4] X.-L. Wei, Y.Z. Wang, S.M. Long, C. Bobeczko, A.J. Epstein, J. Am. Chem. Soc. 118 (1996) 2545.
[5] L.V. Lukachova, E.A. Shkerin, E.A. Puganova, E.E. Karyakina, S.G. Kiseleva, A.V. Orlov, G.P. Karpacheva, A.A. Karyakin, J. Electroanal. Chem. 544 (2003) 59.
[6] A.A. Karyakin, A.K. Strakhova, A.K. Yatsimirsky, J. Electroanal. Chem. 371 (1994) 259.
[7] H. Tang, A. Kitani, S. Ito, Electrochim. Acta 42 (1997) 3421.
[8] H. Tang, A. Kitani, T. Yamashita, S. Ito, Synth. Met. 96 (1998) 43.
[9] Y. Wang, W. Knoll, Anal. Chim. Acta 558 (2006) 150.
[10] M. Liu, M. Ye, Q. Yang, Y. Zhang, Q. Xie, S. Yao, Electrochim. Acta 52 (2006) 342.
[11] J. Schiller, J. Arnhold, J. Schwinn, H. Sprinz, O. Brede, K. Arnold, Free Radic. Res. 30 (1999) 45.
[12] G.-F. Zhang, H.-Y. Chen, Anal. Chim. Acta 419 (2000) 25.
[13] Y.-T. Chang, K.-C. Lin, S.-M. Chen, Electrochim. Acta 51 (2005) 450.
[14] S.-M. Chen, K.-C. Lin, J. Electroanal. Chem. 523 (2002) 93.
[15] K.A. Fahnrich, M. Pravda, G.G. Guilbault, Talanta 54 (2001) 531.
[16] K.-C. Lin, S.-M. Chen, J. Electroanal. Chem. 589 (2006) 52.
[17] V. Ferreira, A.C. Cascalheira, L.M. Abrantes, Thin Solid Films (2007), doi:10.1016/j.tsf.2007.08.004.
[18] S.L. de Albuquerque Maranhão, R.M. Torresi, J. Electrochem. Soc. 146 (1999) 4179.
[19] V. Ferreira, A. Tenreiro, L.M. Abrantes, Sens. Actuators B 119 (2006) 632.
[20] S.-Y. Cui, S.-M. Park, Synth. Met. 105 (1999) 91.
[21] S. Bruckenstein, M. Shay, Electrochim. Acta 30 (1985) 1295.
[22] D.A. Buttry, in: A.J. Bard (Ed.), Electroanalytical Chemistry, vol. 17, Marcel Dekker, New York, 1992.
[23] E.P. Koval'chuck, I.V. Grynchyshyn, O.V. Reshetnyak, R.Y. Gladyshevs'kyj, J. Blazejowski, Eur. Polym. J. 41 (2005) 1315.
[24] E.M. Genies, C. Tsintavis, J. Electroanal. Chem. 195 (1985) 109.
[25] E.M. Genies, A.A. Syed, C. Tsintavis, Mol. Cryst. Liq. Cryst. 121 (1985) 181.
[26] L. Duic, Z. Mandic, S. Kovac, Electrochim. Acta 40 (1995) 1681.
[27] D.E. Stiwell, S.M. Park, J. Electrochem. Soc. 133 (1998) 2254.
[28] N. Pekmez, K. Pekmez, M. Arca, A. Yildiz, J. Electroanal. Chem. 353 (1993) 237.
[29] A.G. Bedekar, S.F. Patil, R.C. Patil, K. Vijayamohanan, Mater. Chem. Phys. 48 (1997) 76.
[30] Y.-B. Shim, M.-S. Won, S.-M. Park, J. Electrochem. Soc. 137 (1990) 538.
[31] D.M. Mohilmer, R.N. Adams, W.J. Argersinger, J. Am. Chem. Soc. 84 (1962) 3618.
[32] E.M. Genies, J.F. Penneau, M. Lapkowski, A. Boyle, J. Electroanal. Chem. 269 (1989) 63.
[33] A.F. Diaz, J.A. Logan, J. Electroanal. Chem. 111 (1980) 111.
[34] W.S. Huang, B.D. Humphrey, A.G. MacDiarmid, J. Chem. Soc., Faraday Trans. 1 82 (1986) 2385.
[35] W.E. Rudzinski, L. Lozano, M. Walker, J. Electrochem. Soc. 137 (1990) 3132.
[36] R.M.Q. Mello, R.M. Torresi, S.I. Córdoba de Torresi, E.A. Ticianelli, Langmuir 16 (2000) 7835.
[37] R. Mazeikiene, A. Malinauskas, Mater. Chem. Phys. 83 (2004) 184.
[38] Q. Wu, Z. Qi, F. Wang, Synth. Met. 105 (1999) 191.
[39] R. Mazeikiene, A. Malinauskas, Synth. Met. 129 (2002) 61.