Electrochemical preparation and characterisation of Poly(Luminol–Aniline) films

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Abstract

Electrochemical polymerisation of luminol (Lum) with aniline (Ani) is carried out potentiodynamically from acidic medium with different monomers concentration ratios. Aniline units incorporation in the polymer structure is observable in the current density/potential profiles of the polymerisation and characterisation, in acidic medium, by the development of two polyaniline (PAni) like redox switching processes with increasing aniline concentration. Poly(Luminol–Aniline) (P(Lum–Ani)) films characterised in acidic medium show electroactive and stable behaviour, in which the redox process ascribed as polyluminol (PLum) type is overlaid with that of PAni displaying pH sensitivity. Unlike PAni films, the P(Lum–Ani) polymer is electroactive and stable in basic medium and a single redox switching process is observed; its redox charge is enhanced with the increase of aniline concentration in the polymerisation solution.
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1. Introduction

Polymer modified electrodes have been widely studied in the last decades due to their potential applicability in a variety of fields such as electrocatalysis, photoelectrochemistry, sensors and biosensors construction [1]. The possibility of producing modified surfaces with the desired characteristics namely chemical and physical stability and potential window for analytical applications are of high interest in these research areas [2]. Monomers as aniline (Ani) [3,4], pyrrole [3,5] and thiophene [3,6] are the most used in surface modification by electropolymerisation.

3-Aminophthalhydrazide or Luminol (Lum), one of the earliest known synthetic compound exhibiting chemiluminescence [7], has been widely used in luminescence and electrochemiluminescence detection in immunoassays with flow injection system and liquid chromatography [2,8]. This monomer can be chemically [9] and electrochemically polymerised [2,8–12]. It can be electropolymerised by potentiostatic and potentiodynamic methods from acidic medium onto different substrates [2,8,10–12]; the electropolymerisation process and properties of the polyluminol (PLum) films has been studied by several techniques [2,8,10–12].

According to the literature, the oxidative electropolymerisation of Lum is similar to Ani [11] and occurs probably through a linkage of a-NH$_2$ group with the *para*-carbon atom of another Lum molecule. The initial step for the Lum electropolymerisation may be the electrochemical oxidation of the NH$_2$ group, with the formation of a cation radical at anodic potentials ($E > 0.90$ V *vs.* Ag/AgCl at pH 1.5). This cation radical, with an unpaired electron, undergoes delocalisation through the Lum and the coupling reaction of the dimer easily takes place. The electrochemical oxidation of the NH$_2$ group in the dimer occurs and the polymerisation coupling reaction proceeds with the oligomer molecule.

In the Lum oxidation two anodic peaks were observed. Although some authors [11] point to the need of a potential above 1 V (*vs.* Ag/AgCl) for the polymerisation of Lum, it has been reported the formation of stable PLum films onto electrode

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surfaces (Au, Pt and glassy carbon) by limiting the anodic potential to the first peak [2]. Moreover, electrochemical quartz crystal microbalance experiments showed, that in the course of the electropolymerisation, the mass deposition begins earlier at 0.80 V at pH 1.5 (vs. Ag/AgCl) [8].

The possibility of a PLum composition similar to polyaniline (PAni) was suggested in the literature, where the fully reduced and the fully oxidised forms of PLum are analogous to the fully reduced and fully oxidised forms of PAni, respectively [8].

In acidic medium a single redox switching process is reported for PLum [2,8,10], with formal potential occurring at about +0.52 V (vs. Ag/AgCl) which has been attributed to the reduced and oxidised forms of PLum [8]. When the anodic limit potential includes the Lum second oxidation peak, two redox processes are observed at +0.35 and +0.55 V (vs. Ag/AgCl) [11]. It has been reported that electrosynthesised PLum films [8], as other polymers [13], are electroactive and stable in solutions in a wide range of pH values. Between pH 1 and 11, the redox switching process presenting a potential shift of −58 mV/pH unit, which is near the Nernst equation slope for the same number of involved protons and electrons. The pH response may also be due to the deprotonation of the PLum–CO–NH–NH–CO-group [8]. On the contrary, PAni films are known as non-conductive and low electroactive in solutions with pH above 4 due to its deprotonation [14,15]. However, some aniline derivatives, which have been used in copolymerisation studies, proved to be able to overcome this PAni disadvantage by the presence of appropriate substituents in the benzene ring. Successful cases are the sulphonated anilines [16–19] and ortho-aminophenol [14,20,21] that due to the intra-chain or intra-molecular proton transfer allow to obtain electroactive polymers in neutral and basic solutions. Moreover, advantage in solutions with pH >4 was taken from the presence in the polymer structure of functional groups, which by exchange of protons between the polymer and the solution allowed the pH adjustment at the copolymer, as the keto–enol equilibria reported for the poly(aniline-co-o-aminophenol) [21].

Copolymerisation provides a convenient synthetic method to prepare materials with desired properties for various applications [14,16,17]. The electrochemical route presents further advantages such as the control of the applied potential and monomer concentration effect on the copolymerisation rate [14,15,19,20,22]. Ani and its derivatives have been used in copolymerisation studies [14–22]. Conductivity, redox couple ion exchange and pH properties of PAni films were modified by copolymerisation of Ani and sulphonated anilines [16–19], carboxylated aniline [15], ortho-methoxyaniline [22] and ortho-aminophenol [14,20,21].

In the literature [1,3,4,23–25] two redox peaks are reported for the PAni redox conversion. The peak at more cathodic potentials has been attributed to the conversion of the fully reduced and insulating leucoemeraldine in the semi-oxidised and conducting emeraldine form and the anodic peak to the conversion of the electronically conducting emeraldine in the fully oxidised and insulating pernigraniline form. An intermediary redox process has been assigned to degradation products of PAni such as benzoquinone/hydroquinone units, which is dependent on the

electrosynthesis conditions, such as anodic potential/synthesis charge and monomer concentration [24,26,27].

Since Lum has been considered an Ani derivative [11] and presents a similar polymerisation process [8,11], the study of both monomers copolymerisation may offer advantages.

The aim of the present work was the electrochemical synthesis of P(Lum–Ani) films from acidic medium in order to achieve polymer modified electrodes with improved redox properties in basic medium.

2. Experimental details

Electrochemical experiments were performed with an IMT102 Electrochemical Interface and a DEA332 Digital Electrochemical Analyser (Radiometer — Copenhagen) connected to a computer for data acquisition (VoltaMaster2 software). A three-compartment cell, with a polycrystalline Au disk working electrode (0.28 cm^2 geometrical area), a Pt foil counter-electrode and a saturated calomel reference electrode (SCE), was used. Before each experiment a mirror-finishing surface was generated by hand-polishing the Au electrode in an aqueous suspension of successively finer grades of alumina (from 5 to 0.05 μm).

Pure polyluminol films were grown in acidic solutions containing 0.5 mmol dm^{-3} of luminol (Fluka) in the interval of potential between 0 and 0.875 V. The polyaniline films were obtained in acidic solutions containing 0.5, 10 and 30 mmol dm^{-3} of aniline (distilled and kept under N$_2$ atmosphere, at 4 °C) in the interval of potential between −0.200 and 0.950 V. The luminol–aniline polymers were grown in the interval of potential between −0.200 and 0.950 V in solutions containing both monomers with different concentration ratios luminol:aniline (1:1, 1:4, 1:20: 1:40 and 1:60); the luminol concentration was kept constant in all experiments (0.5 mmol dm^{-3}). All polymer films were potentiodynamically grown with 10 sweep cycles at a scan rate of $v = 50$ mV s^{-1} in 0.5 mol dm^{-3} H$_2$SO$_4$ (Fluka, p.a.) solutions.

The polymer layers were washed with monomer free solution, H$_2$SO$_4$ 0.5 mol dm^{-3} and characterised electrochemically (by cycling the potential at 50 mV s^{-1}) in solutions with different pH values: H$_2$SO$_4$ 0.1 mol dm^{-3} (pH 1), 0.1 mol dm^{-3} carbonate buffer solutions (potassium carbonate and hydrochloric acid, Merk, p.a.) with pH 8.

The polyluminol, polyaniline and poly(luminol–aniline) films will be referred as PLum, PAni and P(Lum–Ani), respectively, followed by the designation (l:a), which represents the relation between the luminol (0.5 mmol dm^{-3}) and aniline concentrations.

Prior to all measurements the solutions were deaerated with N$_2$ for 15 minutes. All the solutions were prepared with ultra pure water (≥ 18.5 MΩ cm).

3. Results and discussion

3.1. Potentiodynamic electropolymerisation of luminol and aniline in acidic media

The current–voltage behaviour in the course of potentiodynamic electropolymerisation of luminol at a gold electrode (10 cycles, $v = 50$ mV s^{-1}) is presented in Fig. 1.

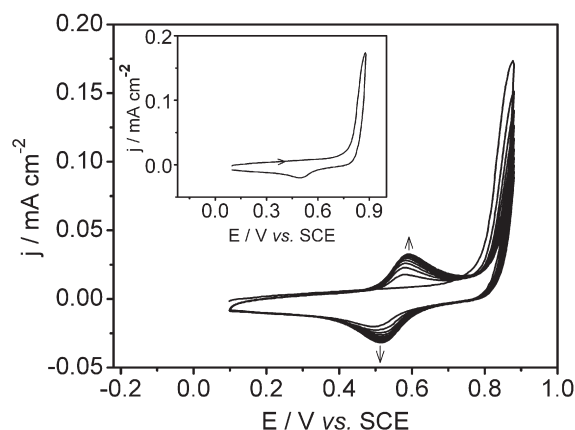Fig. 1. Cyclic voltammograms (10 cycles) of the electropolymerisation of luminol in 0.5 mmol dm^{-3} luminol and 0.5 mol dm^{-3} H$_2$SO$_4$ on gold; $v=50$ mV s^{-1}. Inset: first cycle of the electropolymerisation.

In the first potential cycle (inset of Fig. 1) it is possible to observe that the irreversible oxidation of the Lum monomer occurs at potential values above 0.750 V with formation of cations radical as previously suggested in the literature [8]. In the subsequent sweep cycles, the decrease in the oxidation current at 0.875 V is due to a non-autocatalytic polymer layer deposition on the electrode surface. The anodic and cathodic current density, j, increase at 0.575 and 0.510 V, respectively, indicates the growth of an electroactive PLum film.

The current density of the oxidation peak of the PLum film increase in the first 5 cycles, tending to a plateau in the next potential cycles as shown in Fig. 2, which may be related to the very small increment in the deposited Polymer.

For the potentiodynamic copolymerisation of luminol and aniline, the anodic potential limit was selected from the cyclic voltammograms represented in Fig. 3, considering the oxidation potential of each monomer on gold electrode. Luminol presents two oxidation peaks at 0.875 and 1.035 V as referred in the

Fig. 3. Cyclic voltammograms of (——) luminol (0.5 mmol dm^{-3}) and (—) aniline (0.5 mmol dm^{-3}) in 0.5 mol dm^{-3} H$_2$SO$_4$ on Au electrode; $v=100$ mV s^{-1}.

introduction. The anodic limit of 0.950 V was selected due to the oxidation potential of aniline in the present experimental conditions.

The potentiodynamic electropolymerisation of the P(Lum–Ani) films with different monomer concentration ratios present current/potential profiles comparable to the pure PLum (1:0) films growth (Fig. 1), as illustrated in Fig. 4 for the film P(Lum–Ani) (1:20). The deposition of a polymer layer on the electrode surface makes difficult further monomer oxidation in the subsequent cycles and the current density decreases. At the anodic potential limit (0.950 V), the increase of the oxidation current densities with aniline concentration in the polymerisation solution, due to the simultaneous oxidation of Lum and Ani, can be observed in Fig. 4 ($j_{ox.\ (Lum–Ani)(1:\ 20)}=0.63$ mA cm^{-2} and $j_{ox.\ (Lum)\ (1:60)}=1.85$ mA cm^{-2}, inset in Fig. 4).

In the current response to the potentiodynamic polymerisation, the increase of the oxidation and reduction peaks of the polymer at 0.595 and 0.500 V, respectively, reveals the P(Lum–Ani) film growth and the increase in the aniline concentration leads to the development of a current shoulder at more cathodic
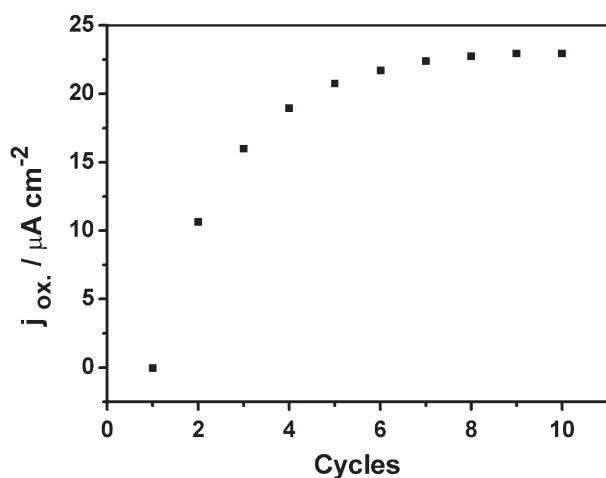

Fig. 2. Oxidation current density increase with potential cycles during the electropolymerisation of luminol (10 cycles, between 0 and 0.875 V) on Au electrode from a 0.5 mmol dm^{-3} luminol in 0.5 mol dm^{-3} H$_2$SO$_4$ solution; $v=50$ mV s^{-1}.
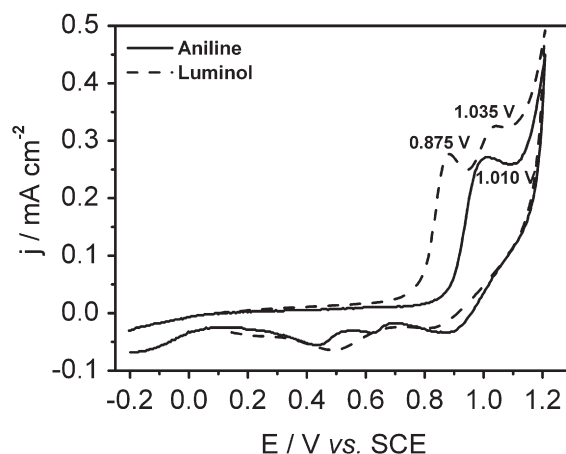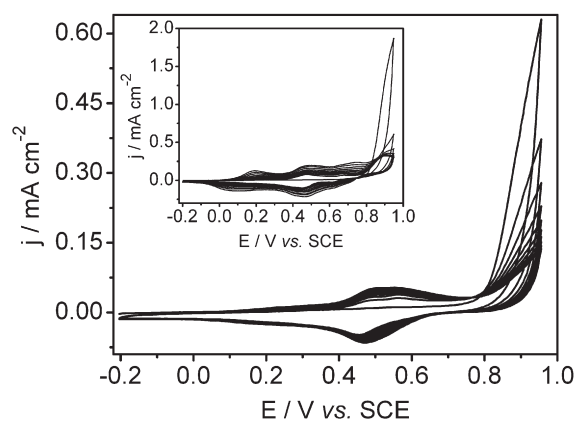

Fig. 4. Cyclic voltammograms (10 cycles) of the electropolymerisation of luminol and aniline in 0.5 mmol dm^{-3} luminol and 10 mmol dm^{-3} aniline (1:20) in 0.5 mol dm^{-3} H$_2$SO$_4$ on gold; $v=50$ mV s^{-1}. Inset: Cyclic voltammograms of the electropolymerisation of luminol and aniline (1:60) in 0.5 mol dm^{-3} H$_2$SO$_4$.
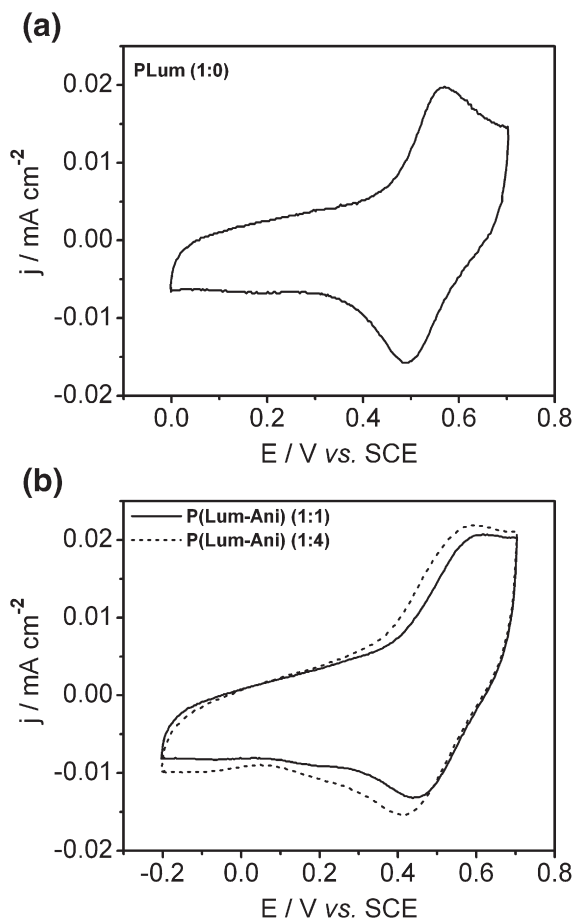
Fig. 5. Cyclic voltammograms of the polymer films characterisation: (a) PLum (1:0) and (b) P(Lum–Ani) (—) (1:1) and (——) (1:4), in H_2SO_4 0.1 mol dm^{-3}; $v = 50$ mV s^{-1}.

potentials, as illustrated in Fig. 4 for the P(Lum–Ani) (1:20) film, which becomes a well defined PAni like oxidation peak at about 0.180 V for the P(Lum–Ani) (1:60) film (inset in Fig. 4).
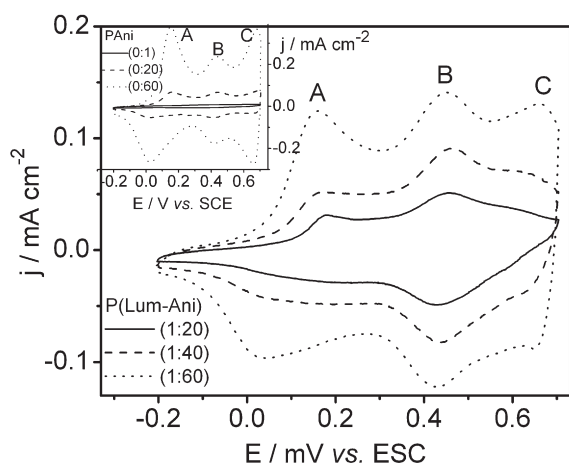

Fig. 6. Cyclic voltammograms of the P(Lum–Ani) films characterisation: (—) (1:20), (——) (1:40) and (·····) (1:60), in H_2SO_4 0.1 mol dm^{-3}; $v = 50$ mV s^{-1}. Inset: PAni (—) (0:1), (—-) (0:20) and (·····) (0:60) (same conditions as for P(Lum–Ani) films).

3.2. Electrochemical characterisation of P(Lum–Ani) films

The electrochemical stability and electroactivity of the P(Lum–Ani) films was evaluated by cyclic voltammetry in 0.1 mol dm^{-3} H_2SO_4 monomer free solution, as shown in Figs. 5 and 6. At low Ani concentration, the P(Lum–Ani) films represented in Fig. 5b show a PLum like behaviour (Fig. 5a), with a single redox peak which moves about 30 mV in the cathodic direction as the monomers concentration ratio changes from (1:1) to (1:4), Table 1. The polymers grown in more concentrated aniline solutions, (1:20), (1:40) and (1:60), Fig. 6, evidence the aniline incorporation in the polymeric structure since PAni like oxidation peaks (A and C) at about 0.160 and 0.660 V, respectively, are observed (Table 1). Under this condition, the presence of luminol in the polymerisation solution apparently inhibits the PAni growth and leads to the formation of Lum–Ani polymers with distinct characteristics from the corresponding PAni (0:20) and (0:60) films (inset in Fig. 6). Peak B, which in the pure PAni films presents lower current density than peaks A and C (inset in Fig. 6), has been assigned to polyaniline degradation products [24,26,27] and may be consequence of the high anodic limit potential ($E_{al} = 0.950$ V) and of the low aniline concentration used in the polymerisation.

P(Lum–Ani) (1:20) and (1:60) films presents lower oxidation and reduction charges and higher current densities of the intermediary peak B (at about 0.450 V) than observed for PAni (0:20) and (0:60) films. A possible explanation for these results is that the simultaneous oxidation of both monomers reduces the

Table 1
Electrochemical data obtained from the voltammograms of the characterisation of polymer films grown under different experimental conditions

Film	E_{al} (mV)	|Lum|:|Ani|	$Q_{ox.}$ (mC cm^{-2})	$Q_{red.}$ (mC cm^{-2})	R	E_p^a (mV)	E_p^c (mV)	ΔE_p (mV)
PLum	875	1:0	0.12	0.11	1.1	570	490	80
P(Lum–Ani)	950	1:1	0.13	0.14	0.93	610	460	150
		1:4	0.15	0.16	0.94	580	434	146
		1:20	0.43	0.42	1.0	181	150^{sh}	–
						452	433	19
		1:40	0.69	0.67	1.0	158	107^{sh}	–
						453	431	22
						607	–	–
		1:60	1.5	1.4	1.1	162	37	125
						455	431	24
						664	650 *	14
PAni	950	0:20	0.73	0.69	1.0	161	15	146
						444	413	31
						692	652	40
		0:60	3.1	2.8	1.1	151	21	130
						431	418	13
						678	660	18

E_{al} — anodic limit potential in the electropolymerisation; Q — oxidation (ox.) and reduction (red.) charges obtained from the polymer films characterisation by cyclic voltammetry at a sweep rate of 50 mV s^{-1}; R — ratio between oxidation and reduction charges; E_p — anodic (a) and cathodic (c) peak potentials; ΔE_p — difference between the anodic and cathodic peak potentials; * — peak near the anodic limit and not well defined; sh — shoulder shape peak.
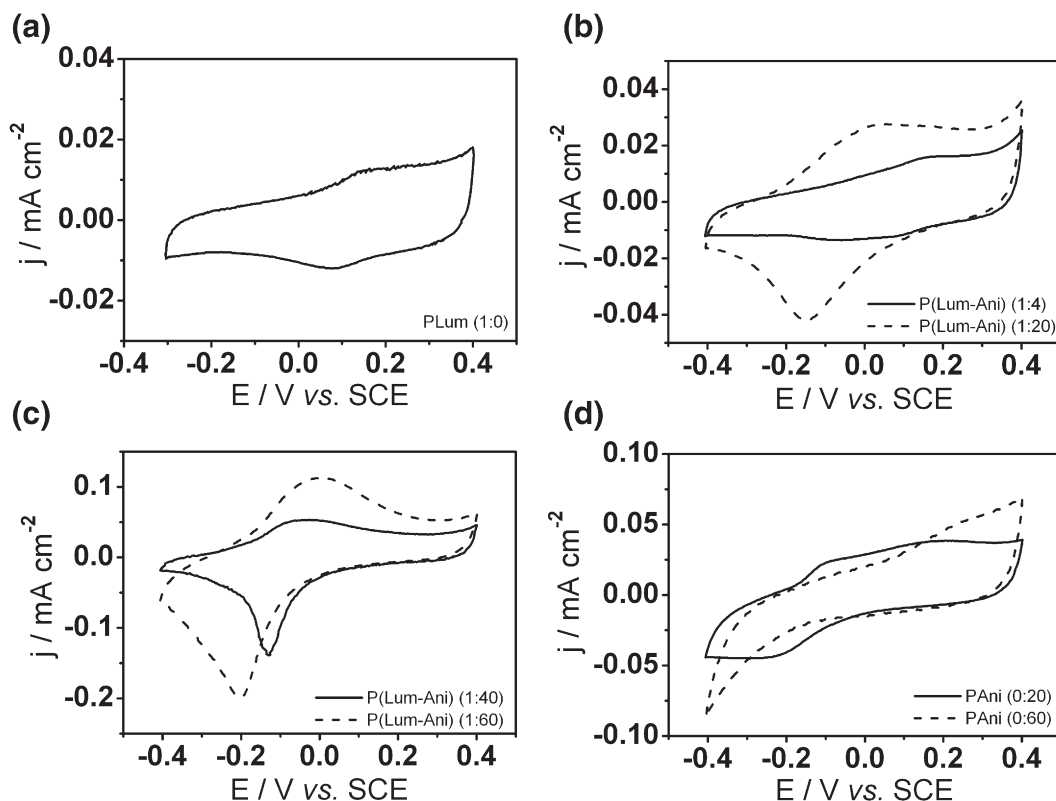
Fig. 7. Cyclic voltammograms of the polymer films characterisation: (a) (—) PLum (1:0), (b) P(Lum–Ani) (—) (1:1) and (——) (1:20), (c) (—) (1:40), and (——) (1:60) and (d) PAni (—) (0:20) and (——) (0:60) in 0.1 mol dm^{-3} carbonate buffer solution (pH 8); $v=50$ mV s^{-1}.

aniline irreversible oxidation since luminol oxidation occurs at lower potential than aniline in this concentration range, Fig. 3. The presence of Lum units in the Lum–Ani polymer chain may reduce the overpotential required for its oxidation when compared with PLum. Accordingly there is a potential shift in the cathodic direction and an increase in the current density of peak B.

In Fig. 7 are represented the cyclic voltammograms (10th cycle) of the characterisation of PLum, P(Lum–Ani) and PAni films in basic carbonate buffer solution (pH 8), from where the electrochemical data compiled in Table 2 was obtained.

The PLum film, Fig. 7a, has low electroactivity however good reversibility in the doping/undoping process was observed in this medium, with a unitary ratio between oxidation and

reduction charges, Table 2. The redox process with 67 mV difference in the oxidation and reduction peaks, suggests a one-electron/one-proton reversible process, Table 2. PLum (1:0) films presents a potential shift of -60 mV/pH unit between pH 1 and 8 (Table 1 and 2), which is in agreement with the Nersnstian value (-59 mV) for a ratio of 1:1 protons and electrons.

Although PAni films present, in basic media (Fig. 7d), a distinct behaviour from that obtained in H$_2$SO$_4$ 0.1 mol dm^{-3} solutions (inset in Fig. 6), P(Lum–Ani) polymers are electroactive and a single oxidation and reduction process is observed in Fig. 7b and c. Similarly to the PLum oxidation peak potential shift (-60 mV/pH), the P(Lum–Ani) films present an oxidation potential decrease of -68 mV/pH unit by considering the

Table 2
Electrochemical data obtained from the voltammograms of the characterisation in carbonate buffer solution with pH 8 of the polymer films grown under different experimental conditions

Film	E_{al} (mV)	|Lum|:|Ani|	Q_{ox} (mC cm^{-2})	Q_{red} (mC cm^{-2})	R	E_p^a (mV)	E_p^c (mV)	ΔE_p (mV)
PLum	875	1:0	0.12	0.12	1.0	150	83	67
P(Lum–Ani)	950	1:4	0.16	0.17	0.94	164	$-70/75^{sh}$	–
		1:20	0.30	0.30	1.0	22	-160	182
		1:40	0.51	0.52	0.98	-30	-130	100
		1:60	0.92	0.95	0.97	-24	-205	181
PAni	950	0:20	0.35	0.35	1.0	$-94/198^{sh}$	≈-230	–
		0:60	0.43	0.42	1.0	–	–	–

E_{al} — anodic limit potential in the electropolymerisation; Q — oxidation (ox.) and reduction (red.) charges obtained from the polymer films characterisation by cyclic voltammetry at a sweep rate of 50 mV s^{-1}; R — ratio between oxidation and reduction charges; E_p — anodic (a) and cathodic (c) peak potentials; ΔE_p — difference between the anodic and cathodic peak potentials; sh — shoulder shape peak.

potential of the middle peak B (acid medium), which, as referred before, may be related to a PLum like process. This remarkable ability of the prepared P(Lum–Ani) films to show electrochemical redox activity in basic medium, resembles the self-doped sulfonated polyanilines behaviour [19].

The presence in the polymer structure of –CO–NH–NH–CO-groups, with pK_a values at 6.35 and 15.21 corresponding to each of the two hydrogen atoms able to dissociate [28], may enable the exchange of protons inside the P(Lum–Ani) films and between the polymer and the surrounding environment, during the redox conversion, allowing the preservation of the films electroactivity. It is noteworthy that is just as the aniline concentration in the polymerisation solution increases that the P(Lum–Ani) films electroactivity also increases in basic medium, Fig. 7 and Table 2. This fact may mean that it is the incorporation of aniline together with the presence of luminol monomeric units in the structure of the polymer, which have the ability to accept/donate protons, what promotes the P(Lum–Ani) films electroactivity in neutral media.

4. Conclusions

Potentiodynamic electropolymerisation of luminol occurs with the increase of the current density of the deposited film, which tends to a plateau after 5 sweep cycles. The P(Lum–Ani) potentiodynamic electrosynthesis in acidic medium depends on the monomers concentration ratio, ranging from a PLum to a PAni like redox behaviour with increasing aniline concentration. Luminol, which is oxidised at lower potential than aniline inhibits the aniline oxidation and consequently affects its incorporation in the film. At high aniline concentration, its incorporation in the polymer structure is evidenced by the development of leucoemeraldine/emeraldine and emeraldine/pernigraniline type processes. A PLum redox process, which is overlaid with PAni degradation products, presents a potential shift of about −68 mV/pH unit in a 1–8 pH range. Unlike PAni, P(Lum–Ani) films are electroactive and stable in basic medium. The presence of proton acceptor/donator groups in the poly(luminol–aniline) structure, as –CO–NH–NH–CO–, seems to be the key to explain the polymer properties in this medium. This polymeric material reveals promising properties for bioelectrochemistry and electrochemiluminescence applications.

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