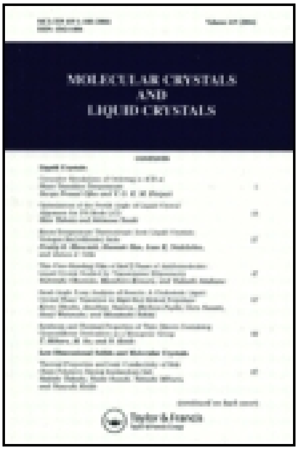

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Influence of the Synthesis Parameters on the Polyluminol Properties

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Influence of the Synthesis Parameters on the Polyluminol Properties

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Polyluminol was synthesized from sulfuric acid aqueous solution (1 to 5 mol L^{-1}) containing luminol (0.5 to 10 mmol L^{-1}) on platinum electrode by cyclic voltammetry. A systematic investigation was performed on the synthesis parameters, resulting in optimized conditions to obtain polyluminol, which are: (i) 2 mol L^{-1} H_2SO_4 aqueous solution; ii) containing 7.5 mmol L^{-1} of luminol; (iii) using thirty potential cycles; (iv) at 100 mVs^{-1}. Preparation parameters and electrosynthesis solutions play important roles in eletropolymerization of polyluminol. In general way, all polyluminol films were electroactives in H_2SO_4 solution independent of synthesis conditions.

Keywords: electrochemical synthesis; luminol; polyluminol

INTRODUCTION

One of most often used classical chemiluminescence agents is luminol, which in presence of hydrogen peroxide and catalyst exhibits the emission with maximum intensity around 425 nm in alkaline medium. The chemiluminescence intensity of luminol increases with the increasing pH of the medium and it dependents on the catalyst being either transition metal or biocatalyst containing hemo-group [1].

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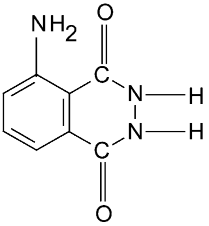


Luminal (3-aminophthalhydrazide)

The polyluminol film formation involves electron transfer on the working electrode to perform oxidation, reduction or both. Chen *et al.* [2] reported the electrodeposition of polyluminol from acid medium containing luminol on different substrates, such as glassy carbon, platinum, gold and tin (IV) oxides electrodes. The polyluminol films demonstrated to be electroactive for NADH oxidation in acidic and neutral aqueous solutions and in a strongly acidic solution, it can electrocatalyzed the oxidation of ephinephrine and dopamine. Epstein *et al.* [3] studied the electrochemical oxidation of luminol in 0.001 mol L^{-1} NaOH solution and they concluded that hydrazide did not "adsorb" on platinum electrodes. Sakura [4] proposed that luminol could adsorb on the platinum in phosphate buffer solution (pH 7.4). Fu *et al.* [5] claim that a polymer of luminol was formed on the surface of a platinum electrode, but they did not detail any discussion. More recently, Zhang *et al.* [6] demonstrated that luminol could polymerize on an electrode surface by constant potential electrolysis ($E = 1.2\,V$ vs. saturated calomel electrode, SCE) or cyclic scan from -0.20 to 1.2 V (vs. SCE). The authors also reported on the electrochemical behavior of luminol and its use as modified electrode for the determination of flavin.

The electrocatalytic properties of polyluminol films are strongly influenced by the synthesis parameters. Despite the fact that in literature the synthesis of polyluminol is described in different acidic media on several substrates [2–6], as far we know no detailed investigation on parameter of polyluminol electrosynthesis has been published. Thus, in this paper the electropolymerization of luminol on platinum by cyclic voltammetry in H_2SO_4 aqueous solutions is described. Also it is reported the investigation of the influence of some synthesis parameters, such as monomer and acid concentrations. The analyses of the electrochemical characteristics of polyluminol films complement these studies.

EXPERIMENTAL

The electropolymerization of luminol in H_2SO_4 on platinum electrode was performed based on the description in reference [2]. The synthesis were performed in one-compartment electrochemical cell with 50 potential cycles by cyclic voltammetry at 100 mV s^{-1}. The working solution was H_2SO_4 aqueous solution containing luminol with concentration varying from 1.0 to 10 mmol L^{-1}. The acids olution concentration changed from 1 to 5 mol L^{-1}. A platinum foil with 0.5 cm^2 surface area was used as working electrode. Two counter electrodes of platinum foil (2 cm × 2 cm) and a reference mercury sulfate electrode (MSE) were used. The potential range used was: i) from -0.45 to $+0.85$ V in the three first cycles for nucleation, and ii) from -0.45 to $+0.55$ V during the following cycles. These potential limits were adopted in order to guarantee the growth of polyluminol films on the electrode surface with minimum degradation.

The electrochemical responses of the films were obtained in H_2SO_4 solutions without monomer at the end of each electrodeposition. The electrochemical responses of the films were obtained using a potentiostat Autolab (PGSTAT20) controlled by GPES 4.9 software for cyclic voltammetry.

RESULTS AND DISCUSSION

Electrochemical Synthesis

The tentative of investigation on luminol electropolymerization in 0.5 and 1 mol L^{-1} H_2SO_4 solutions containing 0.5 or 1 mmol L^{-1} of luminol does not resulted in the synthesis of polyluminol. This is probably due to the low solubility of luminol in acid solutions or to the small thickness of the film on the electrode surface.

Effect Monomer Concentration

Figure 1 shows the cyclic voltammograms for the polyluminol growth from 2 mol L^{-1} H_2SO_4 solution in presence of different luminol concentrations (1.0 to 10 mmol L^{-1}). The magnitude of peak A is a measure of the amount of polymer formed on electrode surface [7]. An increasing in luminol concentration increases the amount of electrodeposited polymer on electrode surface (i.e., peak A). The redox potential shows a small displacement towards more negative values when the luminol concentration is increased. This can indicate that the polymerization rate is favored in presence of low luminol concentration (between 1 to 7.5 mmol L^{-1}).

Dependence of Rate of Polyluminol Formation on Monomer Concentration

The plot of the magnitude of the anodic current peak as a function of the number of potential scans for different luminol concentrations shows that the relationship between the polyluminol growth rate

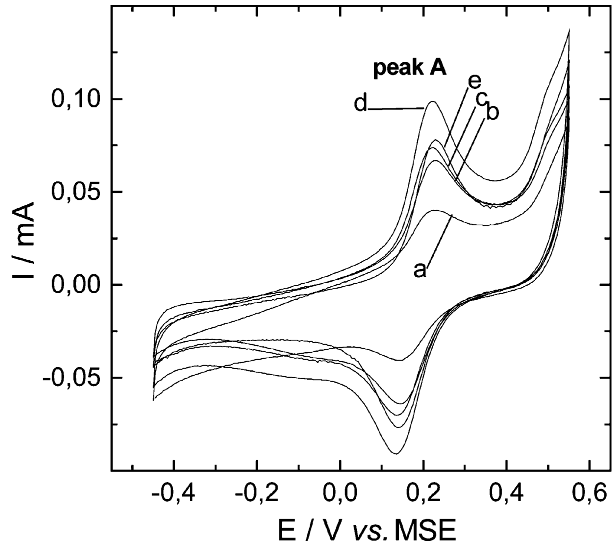


FIGURE 1 50th cyclic voltammograms corresponding to the electrosynthesis of polyluminol on platinum from 2 mol L^{-1} H_2SO_4 aqueous solution containing different luminol concentrations: (a) 1; (b) 2.5; (c) 5; (d) 7.5 and (e) 10 mmol L^{-1}. $v = 100\,mV\,s^{-1}$.

and the luminol concentration; the order of reaction with respect to luminol concentration can be determined [8].

Figure 2 shows the change of current values of peak A (from Fig. 1) with the number of cycles between 0.09 and 0.33 V and a scan rate of 100 mV s^{-1}. The increase of luminol concentration increases the height of peak A. This increase is quick up to the 20th cycle. In the subsequent cycles the polymer presents chemical and physical characteristics that retard the polymerization process.

The polymer growth rate at a certain point can be determined from the slope of the curve at specified points. When the slopes were measured for each luminol concentration at different scan numbers the plots of Figure 3 were obtained. The linearity of these plots indicates that the polyluminol growth rate is first order with respect to luminol concentration in sulfuric acid solution.

Effect of Acid Concentration

Polyluminol films were obtained by electropolymerization from H_2So_4aqueous solutions in different concentrations containing 7.5 mmol L^{-1} luminol, as illustrated in Figure 4. The increasing in

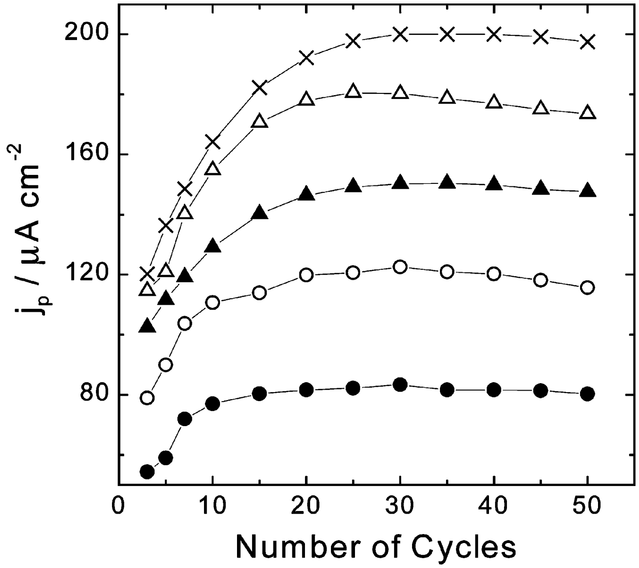


FIGURE 2 Dependence of anodic density current peak on number of potential cycles for various concentrations of luminol: (●) 1, (○) 2.5, (▲) 5, (×) 7.5, and (Δ) 10 mmol L^{-1}. v = 100 mV s^{-1}.

acid concentration increases the current of peak A (i.e., growth rate), which is reducing when the acid concentration was higher than 2 mol L^{-1}. Thus, two different regions can be observed a (i) in lower acid concentration (from 1 to 2 mol L^{-1}): And in (ii) higher acid concentration (from 3 to 5 mol L^{-1}).

It is knowledge that the global polymerization rate is influenced for different rate attributed to process of oxidation, diffusion and adsorption of specimens on surface electrode. At low acid concentration (from 1 to 2 mol L^{-1}) the luminol oxidizes and diffuses easily towards to electrode surface. However, in acid concentration higher (>2 mol L^{-1}) the diffusion process can be retarding or inhibited due to excess of specimens in solution. Thus should occur a competing between luminol cation radical and the ions in solution for the active sites on modifying surface electrode for the presence of polymer. Another evidence of difficulty in electropolymerization process is a small displacement of A peak potential towards to more positive values with the increasing acid concentration.

Figure 5 shows the change of current density values of peak A with the number of cycles when sulfuric acid concentrations changes from 1 to 5 mol L^{-1}.

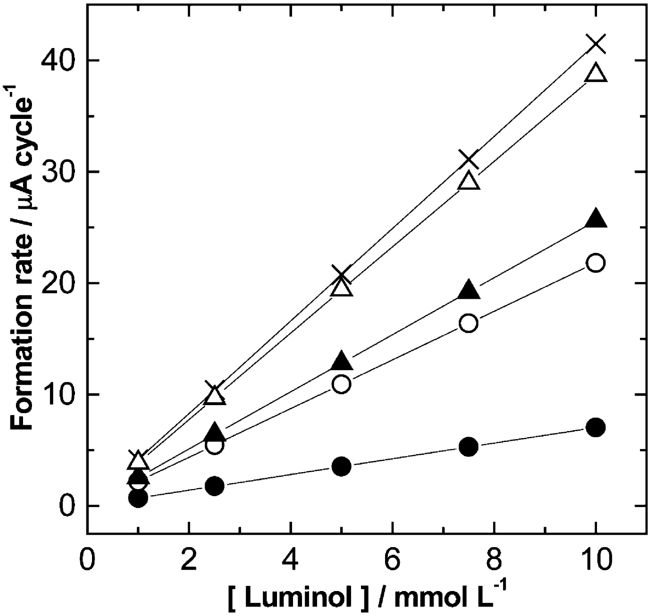


FIGURE 3 Formation rate of polymer values obtained as slope from Figure 3 at various anodic peak current values against concentration of luminol: (●) 1, (○) 2.5, (▲) 5, (×) 7.5, and (Δ) 10 mmol L^{-1}. Supporting electrolyte: 2 mol L^{-1} H_2SO_4.

The increase in sulfuric acid concentration (1 to 2 mol L^{-1}) increases the height of peak A. For acid concentrations higher than 2 mol L^{-1} the polyluminol growth is retarding. The excess of anions in solution can promote the formation of a complex between luminol and species sulfate in solution, which tends to reduce the number of cation radical of luminol in medium.

Electrochemical Behavior

The electrochemical stability of polyluminol films was evaluated by their electrochemical behavior in H_2SO_4 aqueous solution, in which the polymers were obtained and without monomer, as shown in Figure 6. The polyluminol electrochemical response was characterized for one redox process (peaks A/A′) described for Chen *et al.* [2] as: the fully oxidized polyluminol film redox process is shown in the following diagram and it is represented in Figure 6 as peak A.

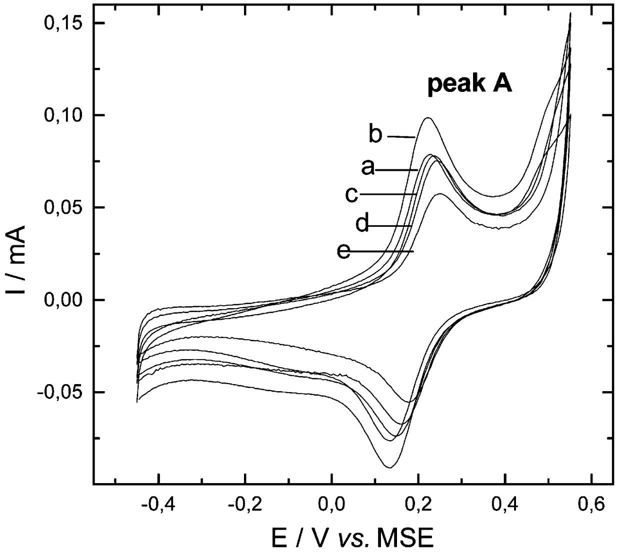


FIGURE 4 Growth voltammograms of polyluminol obtained from 7.5 mmol L^{-1} luminol and H_2SO_4 aqueous solution of different concentrations: (a) 1; (b) 2; (c) 3; (d) 4 and (e) 5 mol L^{-1}.50th cycle.

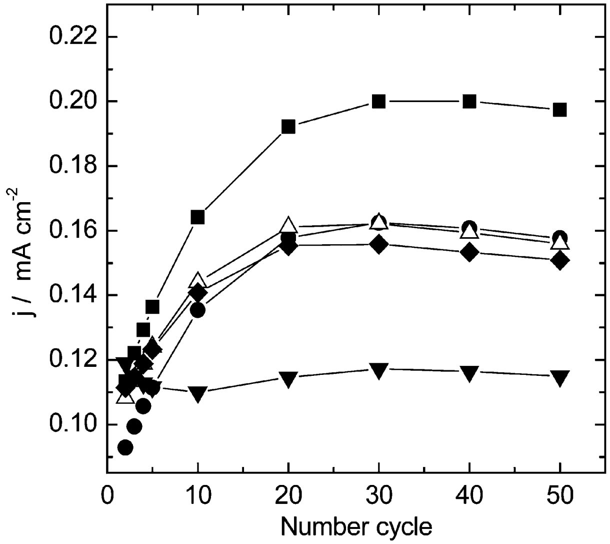
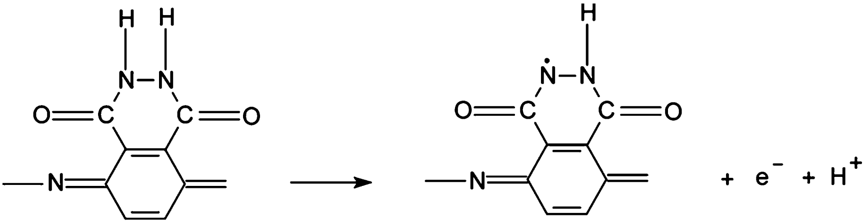
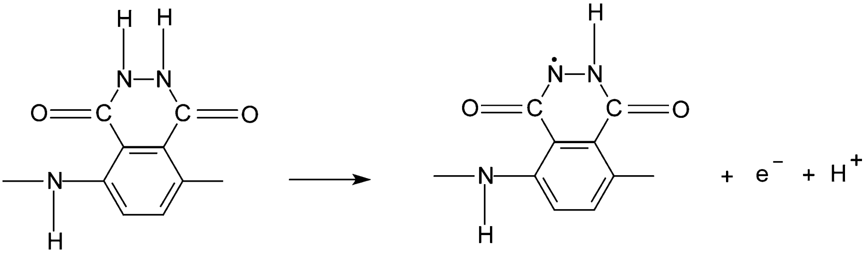


FIGURE 5 Dependence of anodic peak density current on cycle number at various concentrations of acid (H_2SO_4) at a scan rate of 100 mV s^{-1}: (●) 1, (■) 2, (△) 3, (◆) 4, and (▼) 5 mol L^{-1}.



and the fully reduced polyluminol film redox process is shown in the following diagram and it is attributed in Figure 6 as peak A′.



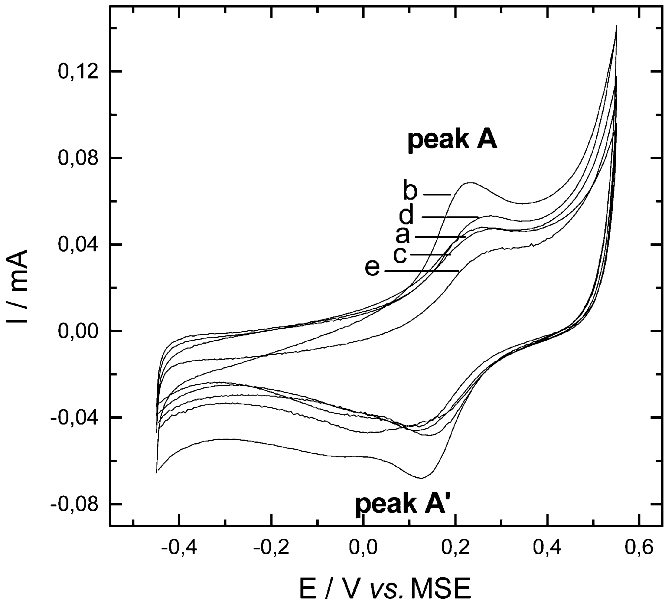


FIGURE 6 Electrochemical response of polyluminol films obtained from different acid aqueous solutions containing 7.5 mmol L^{-1} of luminol. When H_2SO_4 solution concentrations were (a) 1; (b) 2; (c) 3; (d) 4 and (e) 5 mol L^{-1}. Scan rate at 100 mV s^{-1}. Fifth cycle.

In general way, all polyluminol films independent of synthesis conditions (i.e., luminol or acid concentrations) were electroactives in sulfuric acid.

CONCLUSION

Luminol electropolymerization from sulfuric acid aqueous solutions containing luminol on platinum electrode is possible on different conditions. The optimized conditions to obtain polyluminol are: (i) 7.5 mmol L^{-1} of luminol containing in (ii) 2 mol L^{-1} H_2SO_4 solution; (iii) by thirty potential cycles; (iv) at 100 mV s^{-1}. Preparation parameters and solutions electrosynthesis play important role in polyluminol synthesis on solid substrate. The increasing in luminol concentration ($>$7.5 mmol L^{-1}) does not increase polymerization rate. This can be due to excess of specimens in solutions, which should be competing to adsorb on modified electrode surface.

The most important parameter of luminol electropolymerization was the realization of process of nucleation on electrode surface. This affects positively the polymerization process, i.e., accelerating the polymerization rate due to a greater number of nuclei on surface electrode. In general way, all polyluminol films showed to be electroactive in H_2SO_4 solution independent of synthesis conditions.

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