

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 poly(luminol) (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 \AA 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 $7 \mu\text{g}$.

PLum and P(Lum-Ani) films were potentiodynamically grown on the Au working electrode by cycling the potential at $\nu = 50 \text{ mV s}^{-1}$ scan rate, between 0 and 0.875 V versus SCE (poly(luminol) and 0.95 V versus SCE (poly(luminol-aniline))) in a 0.5 mol dm^{-3} H_2SO_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_2SO_4 0.1 mol dm^{-3} and characterised electrochemically (by cycling the potential at 50 mV s^{-1}) in H_2SO_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 poly(luminol) 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 poly(luminol) (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_2SO_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

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