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Electrochemiluminescence of $Ru(bpy)_3^{2+}$ loaded in Nafion Langmuir–Blodgett films: Role of the interfacial ultrathin film

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ABSTRACT

Electrochemiluminescence (ECL) of $Ru(bpy)_3^{2+}$ immobilized at Nafion modified electrodes prepared by the Langmuir–Blodgett (LB) technique is studied in the presence of tri-*n*-propylamine (TPrA). A significant dependence of electrochemical and luminescence signals on the number of Nafion-LB layers is evidenced. The study of the dependence of light emission as a function of the pH, indicates that the maximum emission occurs at pH 8. The competition between $Ru(bpy)_3^{2+}$ and the protonated TPrA for the ion-exchange sites of Nafion can determine whether the light emission occurs inside the LB coatings, at the coating/solution interface or in the solution phase. Finally it is demonstrated that the control of the number of LB layers and the surface pressure allows one to control the amount of $Ru(bpy)_3^{2+}$ loading and, as a consequence, the ECL emission.

1. Introduction

Nafion is perhaps the polymeric electrode coating most widely applied for the easy modification of electrode surfaces. Research started in the 1980s with the pioneering studies in Bard's and other groups [1–3] introduced the possibility to deposit a relatively thin layer (typically between 0.5 and 5 μm thick) of Nafion by recasting the polymer on the surface of the electrode. Thanks to the peculiar self-assembly properties of Nafion in hydrophobic and hydrophilic domains which self-aggregate in clusters [4], Nafion recasted films result stable without requiring any cross-linking or other chemical treatments. This allows one to use Nafion coated electrodes to preconcentrate redox cations, to reject anionic interferences and to protect electrodes surfaces from undesired adsorption and poisoning. Since the first examples, Nafion coated electrodes were applied to a variety of successful electroanalytical applications and constitute the bases for the development of the so-called ion-exchange voltammetry [5–7]. Very recently, new interest in Nafion recasted films derives from their use in polymer fuel cells, where it is used in addition to thick Nafion self-standing membranes [8], as component of the catalyst layer [9] and to suppress fuel crossover [10,11].

The recasting of Nafion on electrodes surfaces is typically performed by microvolume evaporation or spin-coating [6]. Notwithstanding the easiness and wide use of such a coating procedure, it is demonstrated that films of recasted Nafion show properties strongly dependent on recasting parameters such as solvent choice, curing temperature or relative humidity during the drying step [12–14]. Lack of full control on such parameters can cause unsatisfactory reproducibility in the behaviour of the coated electrode [15,16].

In order to overcome these limitations, the deposition of Nafion using the Langmuir–Schaefer (LS) [17] and Langmuir–Blodgett (LB) [18] techniques received recently great attention. First of all, the deposition of Langmuir monolayers on electrodes allows one to build continuous permselective coatings as thin as few nanometers [17–19]. Moreover, it was shown that Nafion LB or Nafion LS films present other peculiar characteristics different from those of recasted Nafion, as recently outlined by electrochemical studies [20,21] also in combination with epifluorescence microscopy [22]. Nafion LB films are indeed very homogeneous and compact [18] and being very thin, they present very short response time to electrochemical switching [22].

It is well known that electrogenerated $Ru(bpy)_3^{3+}$ can react with suitable co-reactants to produce electrochemically induced luminescence (ECL). In most ECL systems, the precursors and reactants are dissolved in solution [23–25], however examples of ECL applications based on the $Ru(bpy)_3^{2+}$ immobilized in Nafion coatings have also been reported [26–31]. The immobilization of

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$Ru(bpy)_3^{2+}$ on a solid electrode can provide several advantages with respect to regeneration and recovery of the catalytic system [1,28,31] as well as for sensors development [30,32].

The success of the $Ru(bpy)_3^{2+}$/amine system, in particular with TPrA (tri-*n*-propylamine), is related to the high photon emission efficiency which allows its applications both in non-aqueous and aqueous solutions [33]. The mechanism involved includes many reactions, such as electrochemical oxidation and/or reduction of the parent species and of the intermediates, chemical decomposition of intermediates, annihilation reactions, acid–base pre- and post-equilibrium [34,35].

ECL of $Ru(bpy)_3^{2+}$ incorporated in Nafion LS films was recently reported in a study where some preliminary results showed a complex dependence of ECL on the number of layers deposited [21]. In the present research we investigate more deeply this subject focusing specifically on the role of Nafion LB film on the ECL process. In particular we examine the effect of the film thickness increased step by step on a nanometric scale. With respect to Ref. [21], in this work we use different methods for the preparation of the monolayer, deposition of the film and immobilization of $Ru(bpy)_3^{2+}$. Moreover, we changed systematically some parameters in order to obtain more precise information on the ECL process.

2. Experimental

2.1. Materials

Tris(2,2′-bipyridyl) ruthenium (II) chloride hexahydrate, potassium nitrate, PBS pH 7.4, tri-*n*-propylamine 99% (TPrA), oxalic acid and Nafion® 117 solution (equivalent weight (EW) 1117, 5% w/v in a mixture of low molecular weight alcohol) were purchased from Sigma–Aldrich. Sodium hydroxide and sodium chloride were purchased from J.T. Baker, absolute ethanol from Carlo Erba Reagents. Stock solutions of Nafion at the required concentration were prepared by proper dilution of the commercial solution with methanol. All solutions were prepared in 18 MΩ water purified using a Milli-Ro plus Milli-Q (Millipore) water purification system. Polished float glass, SiO_2 passivated/Indium Tin Oxide (ITO) was from Delta Technologies, USA (R_s = 4–8 Ω). ITO glass slides were cleaned with Alconox, from Alconox, Inc. USA, and rinsed with Milli-Q water before the transfer of the LB-Nafion film.

2.2. Procedure and instrumentation

2.2.1. LB films

Interfacial films of Nafion were prepared using a Langmuir–Blodgett trough of approximately 2 L volume (Langmuir KSV 2000 trough, KSV Instruments Ltd., Finland). The surface pressure was measured by means of a Wilhelmy balance method with an accuracy of 0.2 mN m^{-1}. A total volume of 300 μL of Nafion 0.05% were spread over the 0.1 M NaCl subphase as three separate aliquots of 100 μL. After each addition the interfacial film was compressed and decompressed up to a final compression after the last addition [36,37]. On the basis of the shape of relevant compression isotherms, typical surface pressures for performing the LB Nafion deposition were 30 mN m^{-1}, however some films were deposited at 20 or 45 mN m^{-1}. The transfer of the Nafion Langmuir monolayer to the ITO substrate began by raising it from the aqueous subphase. The ITO coated with *n* LB layers of Nafion will be indicated in the following as *n*-NLBEs; for instance a 15-NLBE is an ITO substrate coated with 15 LB layers of Nafion.

2.2.2. Electrochemical and electrochemiluminescence measurements

Dynamic electrochemical measurements were performed by a CHI Model 660B or an Autolab PGSTAT100 potentiostats using a standard three-electrodes cell. All potentials were measured and reported with respect to Ag|AgCl (KCl-saturated) reference electrode. The electrode area was 0.126 cm^2.

A Crison GLP 21 pH-meter and an Ingold combined glass electrode were used for pH measurements.

For ECL experiments a special home-made three-electrodes cell was used. The cell was placed in a thick iron dark box acting also as a Faraday cage. The distance between the electrode surface and the optical window was 5 mm. A Hamamatsu R7400U-20 (Shimokanzo, Japan) photon-counting PMT tube operating at 800 V was placed in front of the optical window. The output of the PMT was directed to a LeCroy 9350, 500 MHz oscilloscope (Geneva, Switzerland).

3. Results and discussion

3.1. Role of the ion-exchange on ECL and CV patterns

Fig. 1 (solid line) shows a typical compression isotherm for Nafion obtained using the multiple additions (namely three additions) method described in Section 2. The comparison with the isotherm recorded after just one addition of the same amount of Nafion is given by the dotted line in the same figure. The multiple additions method allows one to reach a higher compression in the Nafion interfacial layer, so that a wide range of deposition surface pressures is available (see Section 3.3). Typically, the transfer of the Nafion layers was performed at 30 mN m^{-1}, as described in Section 2.

The NLBEs so obtained were dipped in solutions containing $Ru(bpy)_3^{2+}$ to be loaded with the electroactive complex. Fig. 2 (solid line – right axis) shows the typical cyclic voltammogram recorded at a 15-NLBE after 10 min equilibration in 0.02 mM $Ru(bpy)_3^{2+}$, that is when the voltammetric signal reached a constant value, significantly higher than the one recorded soon after dipping. The main features of the CV of $Ru(bpy)_3^{2+}$ incorporated in NLBE were analysed previously [22]. Here we focus on the reactions between incorporated $Ru(bpy)_3^{2+}$ and TPrA added in solution as co-reactant. As shown by the dashed line in Fig. 2, when 0.6 mM TPrA is added to the 0.02 mM $Ru(bpy)_3^{2+}$ solution, the oxidation current increases, the anodic peak becomes sigmoidally shaped and the cathodic one disappears; this agrees with the occurrence of the known electrocatalytic process between electrogenerated $Ru(bpy)_3^{3+}$ and TPrA

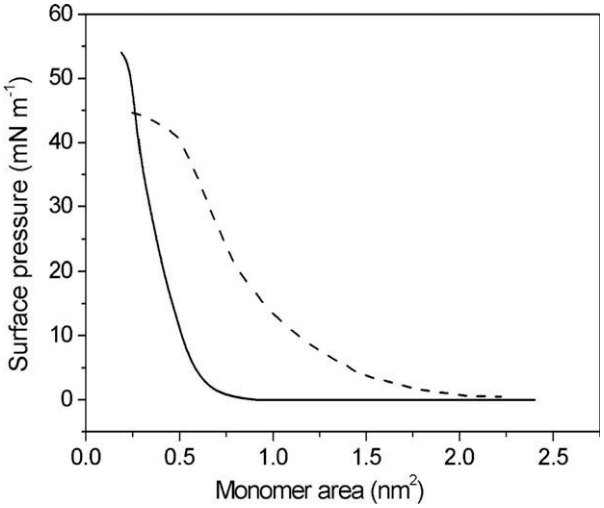

Fig. 1. Surface pressure–monomer area isotherm curves of Nafion using multiple (3 × 100 μL each) additions (solid line) and one single (300 μL) addition (dashed line), subphase 0.1 M NaCl; barrier speed of 12 mm min^{-1}, total volume spread on the trough in each case was 300 μL of a 0.05% Nafion solution in methanol.

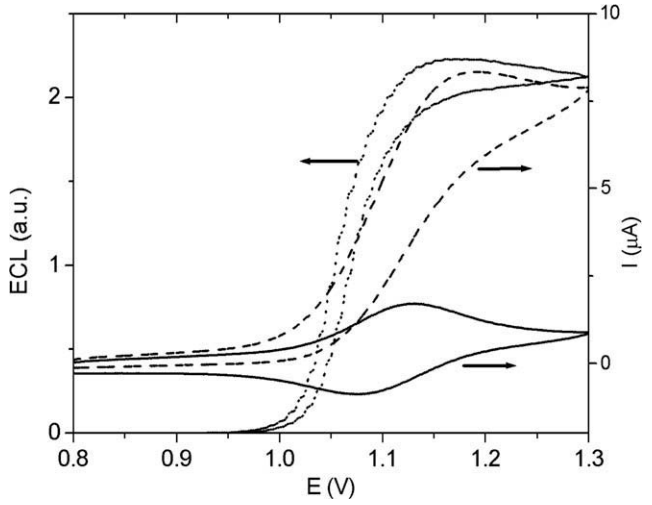

Fig. 2. CVs recorded at a 15-NLBE at 10 mV/s in solution containing 0.024 mM $Ru(bpy)_3^{2+}$, in the absence of TPrA (solid line) and in the presence of 0.6 mM TPrA (dashed line); ECL emission (dotted line) in the same conditions as the dashed line.

[21,38]. As shown by the dotted line (left axis) in Fig. 2, the electrocatalytic signal is associated with a significant ECL emission; indeed, the beginning of the ECL emission is coincident with the foot of the catalytic wave (around 0.95 V), and the pattern of both curves are similar.

The results of the dependence of ECL emission on solution pH are reported in Fig. 3. Maximum ECL emission occurs at pH 8. At acidic pH values, the emission is lower owing to acid–base equilibria [34,35]; at higher pH values the reaction between OH^- and $Ru(bpy)_3^{3+}$ becomes relevant [39] and O_2 formation quenches the excited state producing an overall decrease of the ECL intensity [40]. This trend agrees with previous literature findings at bare electrodes [41]. However the maximum ECL emission is measured at pH ~7 for bare electrodes, and at pH 8 for the NLBE. This slight difference agrees with the lowering of pH caused locally by the H^+ preconcentration capability of Nafion [16].

Data in Fig. 4 show the effect of the $Ru(bpy)_3^{2+}$ loading on CV and ECL signals. Results obtained at bare ITO and at NLBE dipped in solutions with different $Ru(bpy)_3^{2+}$ but at constant TPrA concentration, namely 0.83 mM, are compared (circles for NLBE and triangles for bare ITO). The CV and ECL data both at NLBE and ITO tends asymptotically to a maximum value, such value scaling with the TPrA solution concentration (not shown). At low $Ru(bpy)_3^{2+}$ solution concentrations (approximately <0.2 mM) the increase of both CV and ECL signals with the $Ru(bpy)_3^{2+}$ concentration at the NLBE is dramatically steeper than at the bare ITO. This behaviour indicates that the ECL generating process is an overall second order process, involving both $Ru(bpy)_3^{2+}$ and TPrA solution concentrations. Focusing on the NLBE, the high increase in signals in diluted $Ru(bpy)_3^{2+}$ solutions is clearly a consequence of the $Ru(bpy)_3^{2+}$ preconcentration capability of the Nafion LB coating. Note that partition coefficients of $Ru(bpy)_3^{2+}$ $\left(k_D = \left[Ru(bpy)_3^{2+}\right]_{film} / \left[Ru(bpy)_3^{2+}\right]_{sol}\right)$ as high as 10^7 have been reported for recasted Nafion [42]. In diluted $Ru(bpy)_3^{2+}$ solutions, the ECL generating process involves mainly the $Ru(bpy)_3^{2+}$ preconcentrated in Nafion, since its local concentration is dramatically higher than the $Ru(bpy)_3^{2+}$ solution concentration. On the other hand, at high $Ru(bpy)_3^{2+}$ solution concentration ($\geqslant$1 mM), the Nafion LB coating tends to be saturated, and, in principle, ECL can be produced also by the reaction between $Ru(bpy)_3^{2+}$ in solution and TPrA. Note that under surface saturation conditions, the difference in concentration between $Ru(bpy)_3^{2+}$ in the film and $Ru(bpy)_3^{2+}$ in solution is not so dramatic as in diluted solution. As a consequence, since the efficiency of the ECL emission in the solution phase is higher than in the Nafion LB film (see below), the ECL emission at bare ITOs and at NLBE becomes comparable.

In order to clarify whether the amine is able to penetrate in the Nafion film, CVs experiments were carried out at bare ITO and at

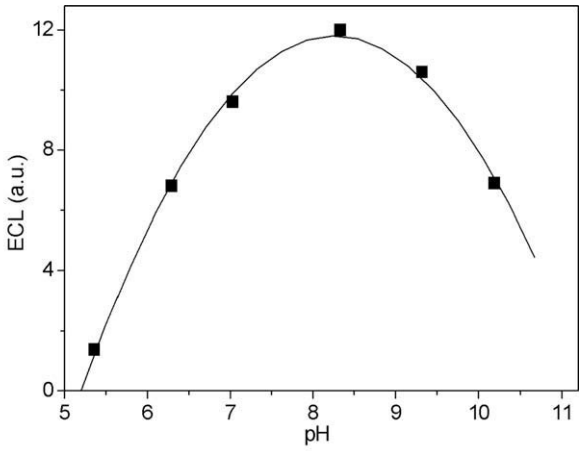

Fig. 3. Variation of ECL emission area with pH at 15-NLBE. Measurements in 0.024 mM $Ru(bpy)_3^{2+}$ and 0.6 mM TPrA PBS solution, scan rate 100 mV/s.

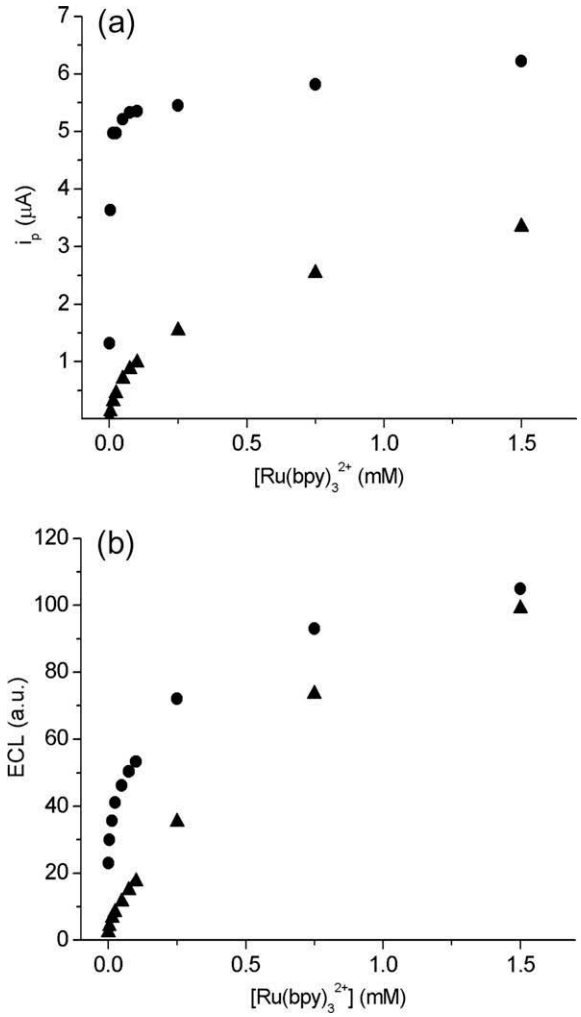

Fig. 4. Peak current (a) and light emission area (b) at 35-NLBE (circles) and bare ITO electrode (triangles) vs. $Ru(bpy)_3^{2+}$ solution concentration, in the presence of 0.83 mM TPrA in 50 mM PBS at pH 7; scan rate, 10 mV/s.

NLBE, testing TPrA as the only analyte present. As shown in Fig. 5, no signal was observed for TPrA at the bare ITO electrode, whilst at the modified electrode TPrA exhibits an irreversible oxidation process at potential values $\geqslant 1.0$ V. The observation of such a process at the NLBE indicates that protonated TPrA can penetrate in the LB-Nafion coating, thanks to ionic attraction with the sulfonated ion-exchange groups of Nafion. Being a monocationic species, protonated TPrA is not expected to really compete with the $Ru(bpy)_3^{2+}$ dication for the ion-exchange sites, since its distribution coefficient is expected to be much smaller than the $Ru(bpy)_3^{2+}$ one; however, we wish to point out that under these conditions, the co-reactant can enter within the coating so that the ECL producing reaction is not localised only at the Nafion/solution interface, but also inside the film.

3.2. Role of the number of LB layers

A peculiarity of the NLBE is that the thickness of the polymer film can be changed in a controlled way, with step increments which can be as small as 2 nm; this figure corresponds indeed to the thickness of 1 Nafion-LB layer. Such a peculiarity allowed us to study in great detail (at levels not available with recasted film) the role of the film thickness on the ECL process.

As outlined by data in Fig. 4, the reaction of $Ru(bpy)_3^{2+}$ with the co-reactant TPrA can indeed take place at different locations, namely, inside the film, at the film/solution interface and in the solution phase. To discriminate among these processes, we focused on the effect of the thickness of the film, i.e., the number of Nafion-LB layers, on the ECL emission. To this aim, ITO electrodes modified with increasing number of NLB layers were loaded with $Ru(bpy)_3^{2+}$. ECL emission was measured after dipping the $Ru(bpy)_3^{2+}$-loaded electrodes in solution with increasing TPrA concentration. In these experiments, ECL values were compared while operating in the presence and in the absence of 1 mM $Ru(bpy)_3^{2+}$ in solution.

Data in Fig. 6a show the dependence of ECL measured with $Ru(bpy)_3^{2+}$ in solution as a function of TPrA concentration at a bare ITO and at coated 3-, 5-, 35-NLBEs. All plots display a common slope at low TPrA concentration (up to 0.05 mM). The evidence that under these experimental conditions the thickness of the film does not change the ECL signal indicates that the emission occurs mainly at the film/solution interface. TPrA cannot reach the inner part of the film because it reacts with the $Ru(bpy)_3^{3+}$ generated in the solution by electron exchange with $Ru(bpy)_3^{3+}$ in the film; this situation is sketched in Fig. 7a. At higher TPrA concentration, ECL at the coated electrode is larger than the one at the bare ITO and scales (although not remarkably) with the number of Nafion-LB layers. Such a dependence indicates that at high concentration, protonated TPrA can enter the LB film. As a consequence, ECL emis-

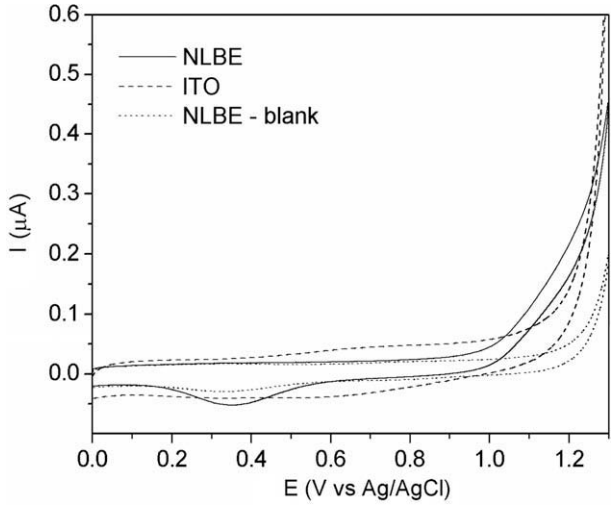

Fig. 5. Cyclic voltammograms recorded at 10 mV/s at bare ITO (dashed line) and 15-NLBE (solid line) in 0.61 mM TPrA 50 mM PBS pH 7; 15-NLBE (dotted line) in pure PBS.

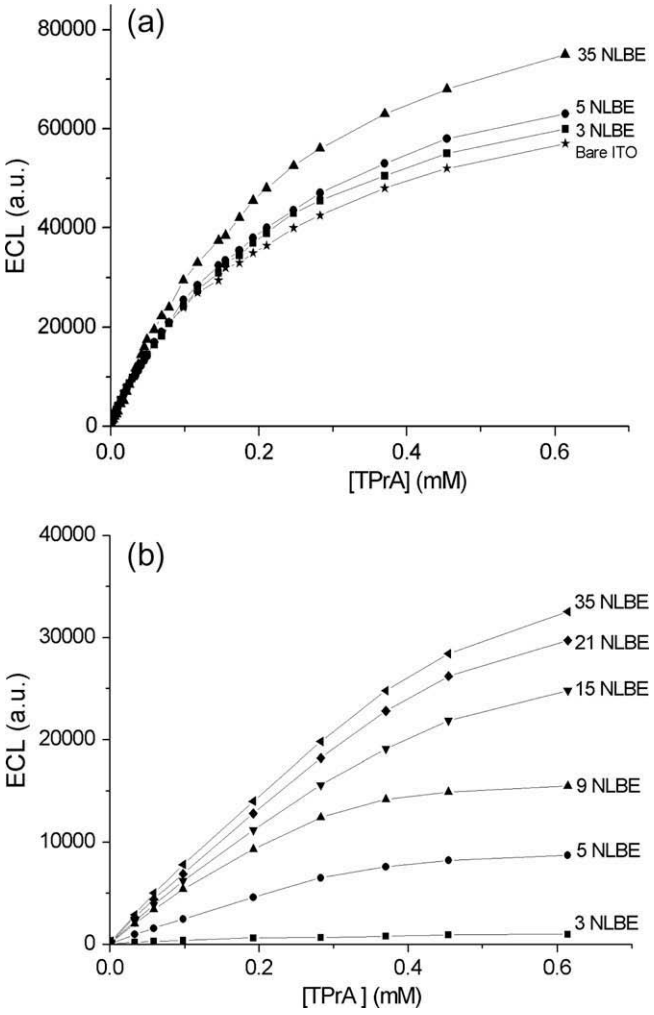

Fig. 6. ECL emission at bare ITO and at NLBE with different number of layers and loaded with $Ru(bpy)_3^{2+}$ as a function of TPrA concentration: (a) measurements in 1 mM $Ru(bpy)_3^{2+}$ 50 mM PBS pH 7 solution; (b) films loaded in 1 mM $Ru(bpy)_3^{2+}$, then washed and transferred in pure 50 mM PBS pH 7 for the measurements.

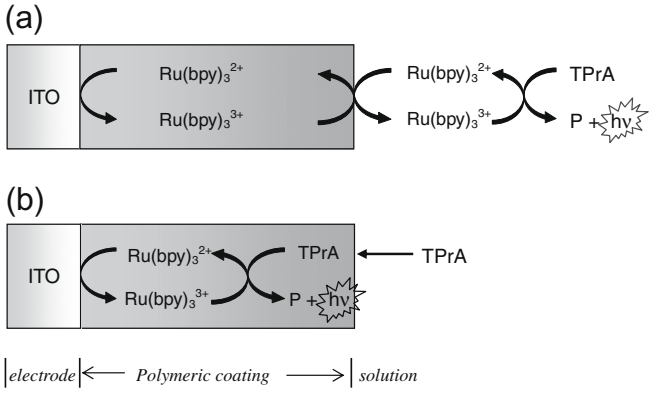

Fig. 7. Simplified scheme sketching the reactions at an NLBE loaded with $Ru(bpy)_3^{2+}$ in the presence (a) and in the absence (b) of $Ru(bpy)_3^{2+}$ in the solution.

sion from the inner coating contributes significantly to the overall signal. When increasing the number of layers from 3 to 35, the ECL emission at a TPrA concentration of 0.6 mM increases indeed of more than 20%.

A completely different situation is observed when the measurements are carried out with $Ru(bpy)_3^{2+}$ present only inside the film, that is with NLBE loaded in $Ru(bpy)_3^{2+}$ solutions, than transferred in buffer to which increasing concentrations of TPrA were added. As reported in a previous paper [22], some slight and slow leaching of $Ru(bpy)_3^{2+}$ occurs after the transfer, however, signals are stable 1 h after the transfer; for this reason, all the measurements reported here were performed after 1 h equilibration time, after transfer in pure supporting electrolyte. Fig. 6b shows that the slopes of these plots depend on the number of Nafion-LB layers also at low TPrA solution concentration. Such a dependence on the number of layers is further stressed at high TPrA solution concentrations. This agrees with an ECL emission dominated by the reactions occurring inside the LB layers (see Fig. 7b). It can be noted that ECL emission at 0.6 mM TPrA solution increases 30 times when passing from a 3-NLBE to a 35-NLBE. It is worth pointing out that the absolute emission with no $Ru(bpy)_3^{2+}$ in solution is lower than with $Ru(bpy)_3^{2+}$ in solution. With no $Ru(bpy)_3^{2+}$ in solution at low thicknesses (<8 layers, i.e., approximately 16 nm [22]), all the $Ru(bpy)_3^{2+}$ incorporated reacts rapidly with the co-reactant. From 9 to 35 layers the process tends to slow down, being limited by the diffusion of the reagents in the (now) thicker coating.

Fig. 8 shows the dependence of ECL emission on the number of Nafion-LB layers, each curve referring to a different TPrA solution concentration. Note that no $Ru(bpy)_3^{2+}$ is present in the solution. These curves show that a plateau is always reached, but it is reached at smaller number of layers the smallest is TPrA solution concentration. This confirms that the incorporation of TPrA in the LB film plays a relevant role. Indeed, the increase in TPrA solution concentration increases both the diffusion rate and the partitioning of TPrA in the coating. However, the latter process is slower for thicker films. A similar trend, at least up to 20 LS-layers, was recently observed also by Bertoncello et al. [21]; however, it was discussed only in terms of slowness of diffusion of the reagent in the solution phase. Data in Fig. 6b indicate that the partitioning and diffusion of TPrA within the coating can not be neglected.

As a comparison, the role of $Ru(bpy)_3^{2+}$ inside the film with respect to ECL was further investigated using a negatively charged co-reactant, namely oxalate. As shown in Fig. 9, at a NLBE loaded with $Ru(bpy)_3^{2+}$ in the presence of oxalate in the solution, ECL emission is observed, however its intensity is dramatically lower than with TPrA (see Fig. 9 – triangles) both at the same concentration. The insert in Fig. 9 shows that the ECL emission measured at a 5-NLBE loaded with $Ru(bpy)_3^{2+}$ depends indeed on oxalate concentration, however its intensity is always remarkably smaller than with TPrA. These results are in agreement with previous literature reports on electrodes modified with recasted Nafion [31], where it was shown that oxalate can not enter in the film because of ionic repulsion by the negatively charged sulfonic groups of Nafion.

The above reported experimental evidences give information on the possible predominant mechanism for the ECL reaction at NLBEs loaded with $Ru(bpy)_3^{2+}$. In particular, they support the occurrence of different reactions which can occur in three different locations: inside the film, at the polymer/solution and in homogeneous solution.

For the case of data in Fig. 6b, the reaction (1) occurs inside the film.

$$Ru(bpy)_3^{3+} + TPrA \rightleftarrows Ru(bpy)_3^{2+} + Products + h\nu \quad (1)$$

When $Ru(bpy)_3^{2+}$ is present in the solution, also reaction at the polymer/solution interface is relevant. In the latter case the ECL generating process (1) is coupled by reaction between $Ru(bpy)_3^{3+}$ electrogenerated in the film and $Ru(bpy)_3^{2+}$ in the solution phase, namely the reaction (2) where subscripts p and s refer to polymer and solution phase, respectively.

$$\left(Ru(bpy)_3^{3+}\right)_p + \left(Ru(bpy)_3^{2+}\right)_s \rightleftarrows \left(Ru(bpy)_3^{2+}\right)_p + \left(Ru(bpy)_3^{3+}\right)_s \quad (2)$$

3.3. Influence of the deposition surface pressure

As shown above in Fig. 1, the Nafion interfacial films can be transferred on the ITO operating at different surface pressure. We exploited this possibility to prepare 15-NLB ITO operating the transfer at different surface pressure, namely, 20, 30 and 45 mN m^{-1}. These electrodes were then dipped and equilibrated in 0.050 mM $Ru(bpy)_3^{2+}$ solution, transferred to pure electrolyte and relevant linear sweep voltammograms are shown in Fig. 10. These data show that peak currents scale with the deposition

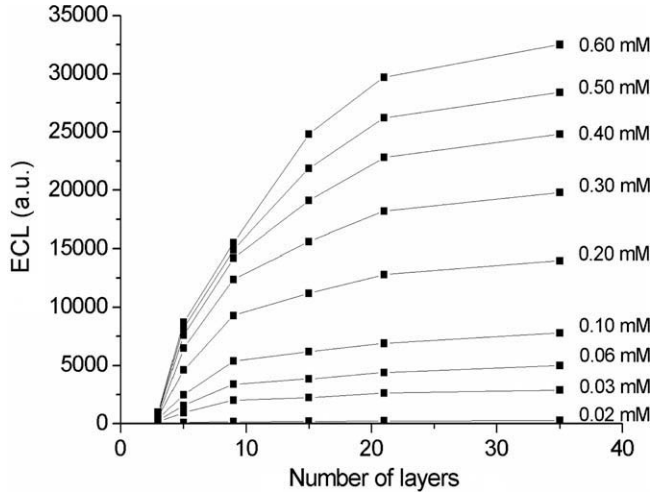

Fig. 8. ECL plot for different number of LB Nafion layers loaded in 1 mM $Ru(bpy)_3^{2+}$ at increasing concentration of TPrA in the solution; measurements performed after transfer in pure supporting electrolyte.

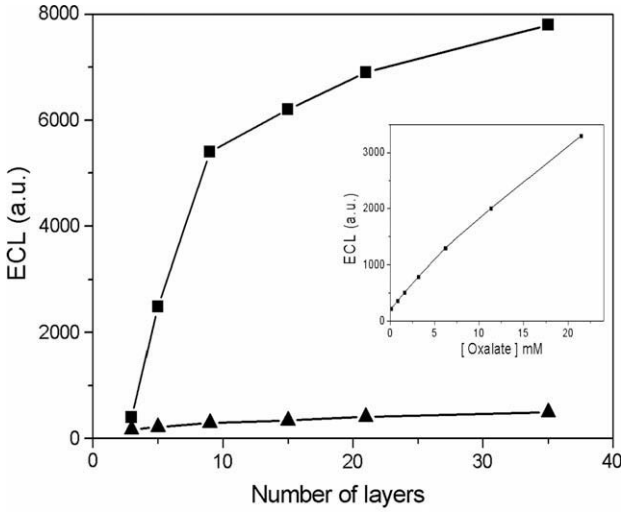

Fig. 9. ECL emission as a function of the number of Nafion-LB layers using as co-reactant: 0.1 mM TPrA (squares); 0.1 M sodium oxalate (triangles). Inset: ECL emission at a 5-NLBE as a function of the oxalate concentration. Experimental conditions: Nafion LB films loaded with 1 mM $Ru(bpy)_3^{2+}$ and measurements performed after transfer in pure supporting electrolyte, 50 mM PBS pH 7 solution.

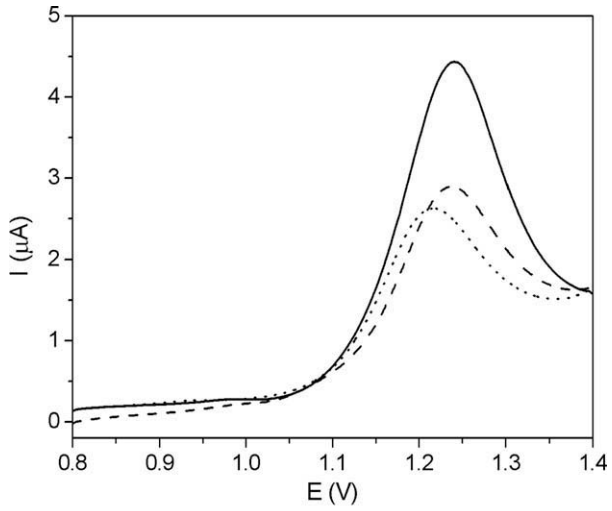

Fig. 10. LSV of $Ru(bpy)_3^{2+}$ loaded in 15-NLBE deposited at a surface pressure of 20 mN m^{-1} (dotted line); 30 mN m^{-1} (dashed line) and 45 mN m^{-1} (solid line), in 0.05 M PBS solution pH 7.0, scan rate 100 mV/s.

surface pressure. Peak current of the solid line curve (45 mN m^{-1}) is indeed almost double than peak current of the dotted line (20 mN m^{-1}), while the dashed line (30 mN m^{-1}) is slightly higher than the dotted one. The increase in peak current could be due to the incorporation of a higher amount of $Ru(bpy)_3^{2+}$ and/or to an increase in the D_{app} values [22]. Anyway, increasing the deposition surface pressure should increase the film compactness with concomitant lowering of the D_{app} [18]. A slight shift in peak potentials towards more positive values is observed for LB films deposited at higher surface pressure. A possible explanation can be the lower water content in the film obtained at higher pressure, this reflecting in a more difficult solvation of the $Ru(bpy)_3^{3+}$ (with higher ionic charge) generated by the oxidation process. Similar behaviour has been reported for the case of $Os(bpy)_3^{2+}$ in recasted Nafion "dried" at different levels [43].

ECL measurements were performed with these 15-NLBEs by dipping the electrodes in solutions with increasing TPrA solution concentration. Fig. 11 compares the trends in ECL emission for these modified electrodes as a function of TPrA solution concentration. The highest signal was obtained with the NLBE prepared at 45 mN m^{-1}, the ECL emission decreasing by decreasing the deposition surface pressure. This evidence indicates that the $Ru(bpy)_3^{2+}$ concentration increases with the surface pressure. Higher surface pressure means a more compact film with a higher surface density of ion-exchange sites and, therefore, capability to incorporate higher amounts of $Ru(bpy)_3^{2+}$. Finally, higher loadings of $Ru(bpy)_3^{2+}$ means higher ECL emission, which is clearly an advantage when thinking to exploit NLBE ITOs for analytical purposes.

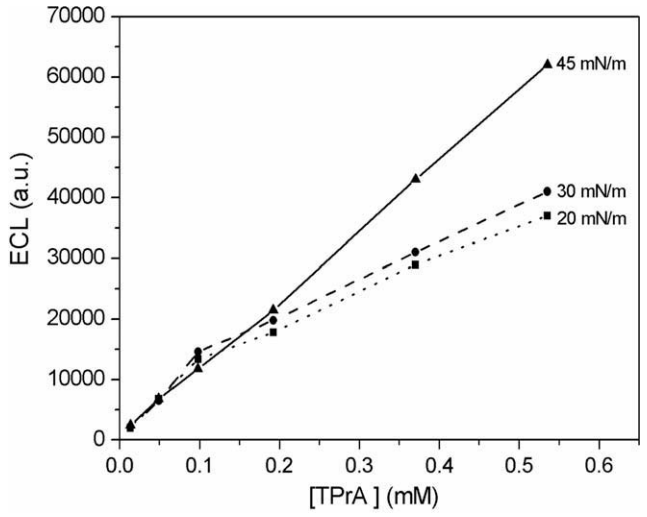

Fig. 11. ECL emission at 15-NLBE deposited at a surface pressure of 20 mN m^{-1} (dotted line); 30 mN m^{-1} (dashed line) and 45 mN m^{-1} (solid line), loaded in 1 mM $Ru(bpy)_3^{2+}$ and measured in pure 0.05 M PBS solution pH 7.0.

4. Conclusions

In this work we demonstrated some interesting aspects concerning the ECL emission of $Ru(bpy)_3^{2+}$ immobilized in the Nafion LB film, in the presence of TPrA as co-reactant. In particular it was observed that ECL emission increases with the number of layers up to reaching a practically constant value for thicker films. This plateau value increases with the TPrA concentration. The role of the Nafion LB film is determinant to hinder the reaction with anionic co-reactants, such as oxalate, while its presence can modify the signal for the case of cationic co-reactants such as protonated TPrA. In the presence of the film, the ECL reactions can take place in different locations depending on the thickness of the film and concentration of $Ru(bpy)_3^{2+}$ and co-reactant. A peculiarity of the NLBE with respect to recasted films is that one can precisely control the amount of incorporated $Ru(bpy)_3^{2+}$ by controlling both the number of Nafion-LB layers deposited and the surface pressure at which the transfer of the Nafion layers is performed. These results are fundamentals for the application of NLBE as ECL amine sensors, which appear very attractive for analytical purposes thanks to the high ECL emission and shorter response time with respect to recasted films.

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