Electrochemical Continuous Emission of $Ru(2,2'\text{-bipyridine})_3^{2+}$ in Polymer Matrix

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Abstract

An electrochemiluminescence (ECL) cell consisting of an indium tin oxide (ITO) anode and two polymer layers of Nafion with tris(2,2'-bipyridine)ruthenium(II) and water-soluble AQ-NYLON with supporting electrolytes was assembled. The polymer layers were swollen with a 5/2/3 mixture of propylene carbonate/N,N-dimethylacetamide/H_2O containing tetra-n-butylammonium perchlorate. When an Al or Pt plate was used as a cathode, the ECL at the polymer layer was observed, but not observed when ITO was used as a cathode. The ECL intensity of the polymer cells was evaluated by changing the applied voltage and frequency.

1 INTRODUCTION

The phenomenon of electrochemiluminescence (ECL), which is due to the generation of luminescent excited states via an electron-transfer reaction of the electrogenerated intermediates, has been extensively investigated for tris(2,2'-bipyridine)-ruthenium(II) ($Ru(bpy)_3{}^{2+}$) in aprotic solvent (1-7) and in polymer electrode (8~12). In these investigations, the ECL was driven by the application of an alternative voltage. As compared with these reports, we obtained the continuous emission with a dc voltage to be applied to the two-electrode cell consisting of a large sheet cathode and a Pt wire anode in a solution(13,14). The emitting location was restricted over the cathode surface. The applied voltage of 10 V was sufficient to obtain the dc ECL. The low driving voltage and the large emitting area are of great advantage for the application to display devices. However, the dc ECL in the liquid system has some problems for fabricating the devices. Then, we studied the dc ECL of $Ru(bpy)_3{}^{2+}$ incorporated into a Nafion ion-exchange polymer film which coats the cathode surface. In our previous studies of the liquid cell, water was found to be essential for the appearance of the dc ECL. Therefore, the Nafion film was coated with a water soluble polymer (AQ-NYLON) which contained H_2O and two kinds of supporting electrolyte, tetra-n-butylammonium perchlorate (TBAP) and LiCl. By using these double-layered polymer matrix as ion transport media, we fabricated a quasi-solid state dc ECL device.

2 EXPERIMENTAL

2.1 MATERIALS.

Tris(2,2'-bipyridine)ruthenium(II) chloride ($Ru(bpy)_3Cl_2$ $6H_2O$), obtained from Aldrich Chemical Co., was recrystallized three times from distilled water and dried in vacuum. Perfluorinated ion-exchange powder (Nafion 117, 1100g/equivalent of proton) was obtained from Aldrich Chemical Co. as 5 wt% lower-aliphatic-alcohol solution with 10 % water. AQ-NYLON (type T-70) was supplied by Toray Industries, Inc. Chemical structure of AQ-NYLON is represented by Eq. (1).

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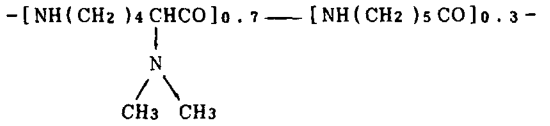

$$-[NH(CH_2)_4\underset{\underset{CH_3\ \ CH_3}{N}}{CH}CO]_{0.7}-[NH(CH_2)_5CO]_{0.3}- \qquad (1)$$

Propylene carbonate (PC, extra pure reagent) and N,N-dimethylacetamide (DMAA, guaranteed reagent) obtained from Nakarai Chemicals, Ltd. were dried with molecular sieve followed by vacuum distillation. LiCl (guaranteed reagent) and TBAP (polarographic grade) obtained from Nakarai Chemicals were used without further purification. An Al sheet (0.08-mm thick) obtained from Tokai Kinzoku Co. Ltd., was washed with acetone and subsequently with distilled water. A Pt sheet (0.023-mm thick), from Itimura Metal Co. Ltd., was rinsed with a 1.2-M HCl solution and subsequently with distilled water before the use.

2.2 PREPARATION OF CELL

Two polymer solutions were prepared as follows. (I) 3.2 mg of $Ru(bpy)_3Cl_2$ was dissolved in 0.1 mL distilled water, then the solution was mixed with 0.9 mL of the 5 wt% Nafion alcoholic solution. (II) 0.5 g of AQ-NYLON and 0.215 g of LiCl were mixed and dissolved in 1 mL distilled water. Five μL of I was spread over the substrate, such as an Al sheet, a Pt sheet, and an indium tin oxide (ITO) glass, and dried in vacuum. The resulting Nafion layer has a thickness of about 1 μm and contains 2.5×10^{-8} mol $Ru(bpy)_3^{2+}$ as calculated. On the dried Nafion/$Ru(bpy)_3^{2+}$ layer a part of II was spread and dried again in vacuum. The obtained polymer-coated electrode was soaked in a mixture of 50 v/v% PC, 30 v/v% H_2O, and 20 v/v% DMAA containing 0.1 M TBAP, then both Nafion and AQ-NYLON layers were swollen. After the surface of the polymer matrix was wiped out with a soft paper to remove excess solution, ITO glass was placed on it as illustrated in Fig. 1. Since the wet AQ-NYLON is adhesive, the ITO counter electrode was fixed to the coated electrode forming a durable solid cell.

2.3 PROCEDURES

For the measurements of the ECL emission, a voltage was applied between the cathode by using a potentiostat (Toho Technical Research, Type 2090) which was connected to a function generator (Leader, LFG-1300). The reference terminal of the potentiostat was connected with the ITO counter electrode. The light of the ECL was passed through a grating monochromator (Ritsu, MC-25N) and detected by a photomultiplier (Hamamatsu Photonics, R928). In the course of the ECL experiments, the ECL light intensity at 610 nm was measured as a function of the applied voltage and the duration. The potential of 0 and 3.5 V was applied alternatively and the ECL intensity and current were observed as a function of time. The effect of the applied frequency on the ECL intensity was also measured.

3. RESULTS AND DISCUSSION

The emission was observed, when the dc voltage of few volts was applied to the cell illustrated in Fig. 1. As a cathode the Al or Pt plate can be used for the dc ECL cell, but the ITO glass did not work. Here, we used a 5/2/3 mixture of PC/DMAA/H_2O as a solvent. The ECL was not observed in the absence of water similarly to the case of the liquid cell (13,14). DMAA was contained in the mixture for allowing the dissolution of H_2O in PC (14).

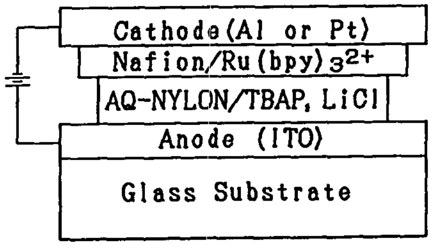

Figure 1. Cross-Sectional view of the ECL cell

The spectrum of the dc ECL shows a maximum intensity at 610 nm, and coincides with that observed with the photoexcitation at 450 nm. Therefore, it is concluded that the dc ECL in the polymer cell originates from the triplet state of $Ru(bpy)_3{}^{2+}$ (3) similarly to the case of the liquid cell (13).

The emission mechanism of the electrochemiluminescence, which was studied in the previous reports (13,14), can be summarized as follows. Since the emission was observed at the cathodic polarization, $Ru(bpy)_3{}^{+}$ is produced by the reduction of $Ru(bpy)_3{}^{2+}$ at the cathode (1), that is,

$$Ru(bpy)_3{}^{2+} + e^- \longrightarrow Ru(bpy)_3{}^{+} \qquad (2)$$

Since water and oxygen were essential to observe the emission, HO_2 may be formed as a cathodic process of oxygen in water (15,16).

$$H^+ + O_2 + e^- \longrightarrow HO_2 \qquad (3)$$

Then, the both reduction products react each other and a emitting species $Ru(bpy)_3{}^{2+*}$ is generated as expressed by Eq. (4).

$$Ru(bpy)_3{}^{+} + HO_2 + H^+ \longrightarrow Ru(bpy)_3{}^{2+*} + H_2O_2 \qquad (4)$$

Here, the difference of the redox potentials of $Ru(bpy)_3{}^{2+/+}$ and $HO_2 + H^+/H_2O_2$ in aqueous solution is lager than the excitation energy for $Ru(bpy)_3{}^{2+}$ (14). Although the redox potentials may differ from those in the polymer matrix, $Ru(bpy)_3{}^{2+*}$ is expected to be formed in the matrix by the reaction (4), similarly to the case of the liquid cell (14).

When the Nafion layer containing both $Ru(bpy)_3{}^{2+}$ and electrolyte was solely used, the dc ECL was not observed. Less hydrophilic properties of the Nafion may be responsible for the absence of emission. Also, the dc ECL was not observed when only LiCl was used as a supporting electrolyte, suggesting that the low dissociation of the salt in the organic solvent. When TBAP was used in place of LiCl, the ECL was slightly observed. In order to obtain the intense emission with a high conductance, both supporting electrolytes, LiCl and TBAP, were used in the following experiments.

Figure 2 shows the relationship between the dc-ECL intensity and the applied voltage at the Al and Pt cathodes. The threshold voltages for the emission at the Al and Pt cathodes were 2.4 V and 1.3 V, respectively. The intensity increased with the applied voltage, and showed the maximum values at 3.2 V and 2.4 V for the Al and Pt cathode, respectively. At a higher voltage, the intensity decreased for the both cathodes. The decrease may be responsible for a lower diffusion rate in the polymer matrix. The maximum intensity was about 10 times higher than that observed for the liquid system (14) although the quantitative absolute value has not been measured.

The difference in the threshold voltage for dc-ECL appearance was also observed in the previous liquid-cell experiment (14). When a three-electrode cell was used to control cathodic potential, the emission began to appear at -1.9 V and -1.6 V vs Ag/Ag^+ for the Al and Pt electrodes, respectively. Then, the difference in the threshold voltage observed in the two-electrode was attributed to the difference in the

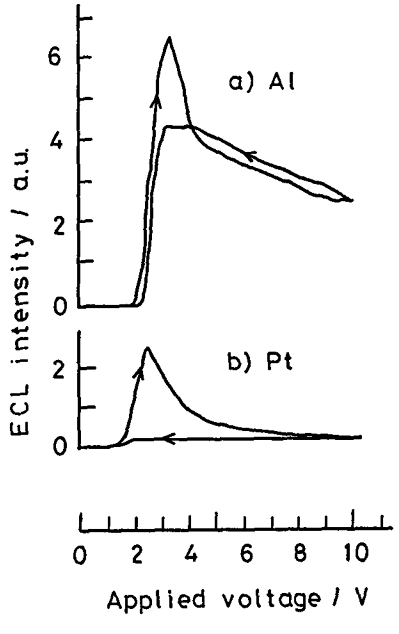

Figure 2. ECL intensity vs. applied voltage curves at (a) Al and (b) Pt cathodes in polymer cell; monitored at 610 nm; scan rate, 40 mV/sec.

effective potential at the cathode. Therefore the difference in the threshold voltage of the polymer cell as shown in Fig.2 may be also responsible for the different effective potentials which are affected by the standard potentials of the electrode materials.

In order to evaluate the duration time of the continuous emission, a time profile of the dc ECL was measured. As shown in Fig. 3, a peak of the luminescence intensity was appeared immediately after the voltage application. Then, the intensity decayed gradually to a constant value in several minutes and sustained for several hours. A high stability of the luminescence was observed in comparison with the liquid system reported previously (13,14).

The change in the ECL intensity with a frequency of applied square wave is shown in Fig. 4. The ECL intensity increases with the frequency up to 0.4 Hz where a maximum value was observed. Above this frequency the intensity decreases abruptly. Slower repetition than 2 Hz is required for the intense ECL emission. In order to elucidate the decrease of the emission above 2 Hz, time profiles of the emission intensity and the current were measured, where the alternative voltage between 0 and 3.5 V was applied. As shown in Fig. 5, the emission intensity increased after the application of the voltage, while the current showed a peak without delay. The ECL intensity reached a maximum value in 0.6 sec (Fig. 5c). When the applied voltage of 3.5 V was changed to 0 V, the reverse current was observed as shown in Fig. 5b. This means that the reduced species, $Ru(bpy)_3^+$ and/or HO_2, release the electron to the cathode, that is, reverse reactions of Eq. (2) and (3) may occur at 0 V. When the voltage of 3.5 V was applied again, it took 0.6 sec to get ECL appearance. Consequently, a time for production of $Ru(bpy)_3^{2+*}$ via a redox reaction between $Ru(bpy)_3^+$ and HO_2 in the diffusion layer required 0.6 sec, whereas the delay was not observed in the liquid system (13). This may be explained by a difference in diffusion constants. The diffusion constants for rubrene in the liquid system and for $Ru(bpy)_3^{2+}$ incorporated in the Nafion matrix were reported to be 3.1×10^{-6} (17) and 5×10^{-10} cm^2/sec (12), respectively. Since the diffusion process in Eq. (4) is probably the rate-determining step in the reaction sequence, the very small diffusion constant by a factor of four orders may be responsible for the slower ECL appearance in the polymer matrix. When the interval of the applied voltage was shorter than 0.6 sec, or when the applied frequency is higher than 1.67 Hz, only a small potion of the reductants encountered each other and the ECL emission became weak as was observed in Fig. 4.

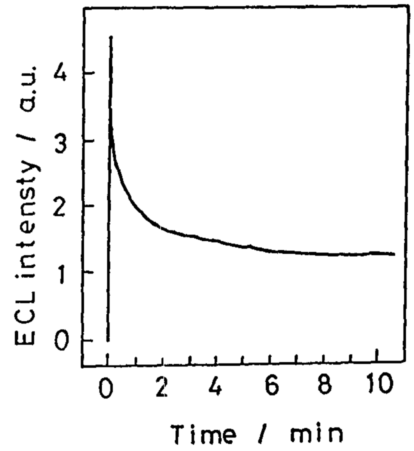

Figure 3. Time profile of dc ECL intensity in polymer; applied voltage, 3.5 V; Al cathode was employed.

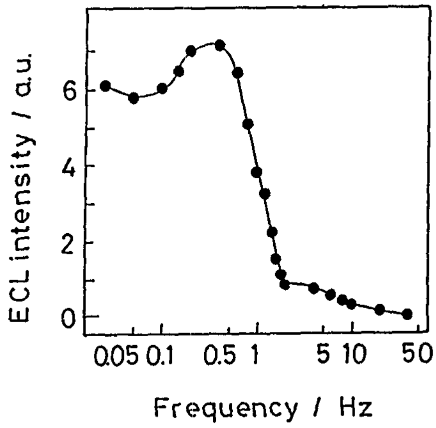

Figure 4. Variation of ECL intensity with frequency of square-wave applied voltage between 0 and 3.5 V.

4. CONCLUSION

The electrochemiluminescence was observed by applying a dc voltage to the cell which consists of the Al or Pt cathode, the Nafion layer containing $Ru(bpy)_3^{2+}$, the AQ-NYLON layer containing TBAP and LiCl as supporting electrolytes, and the ITO anode. The threshold values of the applied voltages for emission were 2.4 V and 1.3 V for the Al and Pt cathodes, respectively. Both the voltages are smaller than those required in the liquid system. Furthermore, ECL intensities are higher and more stable than those observed for the liquid cell. However, the response to the periodical voltage application was not improved for the polymer cell compared with that for the liquid cell at which no delay in the ECL appearance was observed.

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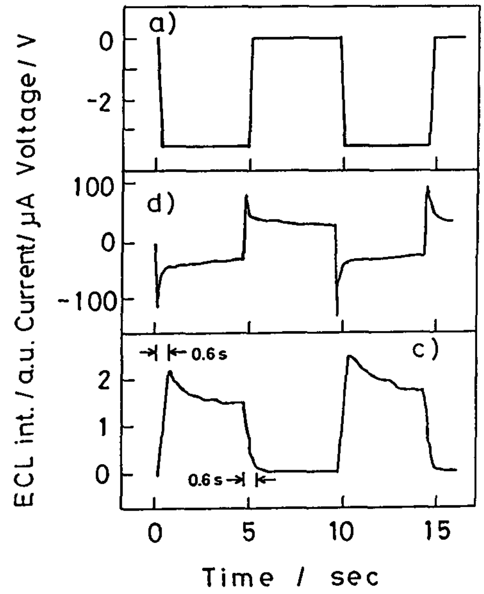

Figure 5. Time profile of (a) applied voltage against ITO anode, (b) current, and (c) ECL intensity in polymer cell; applied voltage, 0 and 3.5 V; applied frequency, 0.1 Hz; Al cathode was employed.

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