

# Effect of Electrode Modification by Polyion Adsorption on Electrochemiluminescence of Luminol

Yasuo Yoshimi, Akitoshi Hatamochi, Kamada Masayuki and Shin-ichi Sekine

Department of Applied Chemistry, Shibaura Institute of Technology, Tokyo, Japan

## 1. INTRODUCTION

Electrochemiluminescence (ECL) of luminol is useful for simple and stable determination of hydrogen peroxide<sup>1</sup>, which is applicable for determination of many kinds of biochemicals by using respective oxidases. Then, the method is feasible for microanalysis of biochemicals in body fluids for therapeutic system. However, it has disadvantage of low sensitivity in mild pH and serious inhibitory by anionic reducers, especially uric acid and ascorbic acid. We have reported that electrode modification by double adsorption of polycation and polyanion increases the sensitivity of hydrogen peroxide by the ECL method in mild pH<sup>2</sup>. However, the adsorption promotes the inhibitory by the anionic reducers. In this work, we speculated the effect of the polymer layers of the ECL of luminol.

## 2. EXPERIMENTAL

### 2.1. Electrode modification

Indium tin oxide (ITO) sputtered glass was used as a working electrode. The surface of ITO was modified with soaking in aqueous solution of polyethyleneimine (PEI) and subsequently in solution of polyacrylic acid. (The electrode is referred to as PAA-PEI-ITO).

### 2.2. Cyclic voltametry

A traditional cyclic voltammetry of uric acid or ascorbic acid was performed with a working electrode of unmodified ITO and PAA-PEI-ITO.

### 2.3. Measurement of ECL

ECL flow cell shown in **Fig. 1** was used as the measurement of the ECL of luminol. Sample solution (1 mM luminol, 0 or 10  $\mu$ M hydrogen peroxide, and 0.1M phosphate buffer saline at pH 7.4) was allowed to flow into the ECL flow cell. A pulsative potential of the electrode was applied 1.0 V for 3 s and 0.0 V for 3 s, stepwisely. The intensity of ECL was detected by a photon counter.

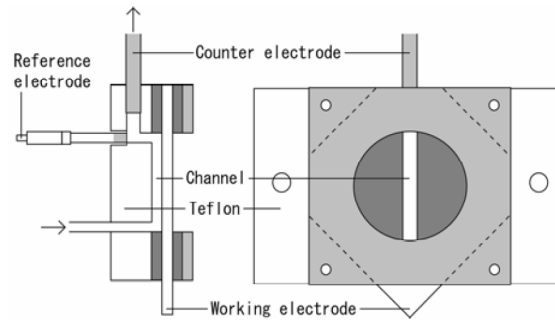


Fig. 1: ECL flow cell

The ECLs with  $10\ \mu\text{M}$  and  $0\ \mu\text{M}$  and hydrogen peroxide were referred to as Signal ECL and Blank ECL, respectively as shown in Fig. 2. The ratio of the two ECLs (S/B ratio) was calculated. The effect of  $10\text{g/dl}$  dye (eosin yellowish or beet red) on the S/B ratio was estimated.

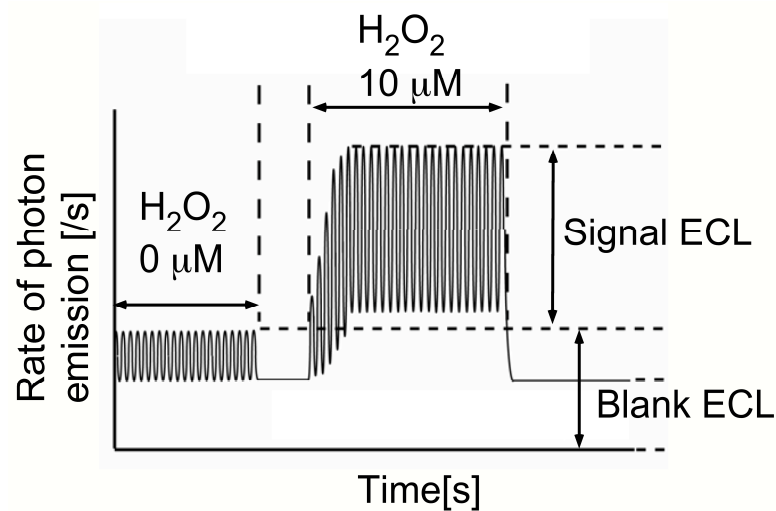


Fig. 2: Analysis of ECL intensity

### 3. RESULTS

#### 3.1. Blocking of anionic reducers by polyionlayer

The cyclic voltammograms of uric acid and ascorbic acid are shown in Fig. 3 and Fig. 4, respectively. The anodic peak of the anionic reducer at PAA-PEI-ITO is disappeared. This results show that the PAA layer on the ITO can block the approach of the anionic reducer toward the electrode effectively.

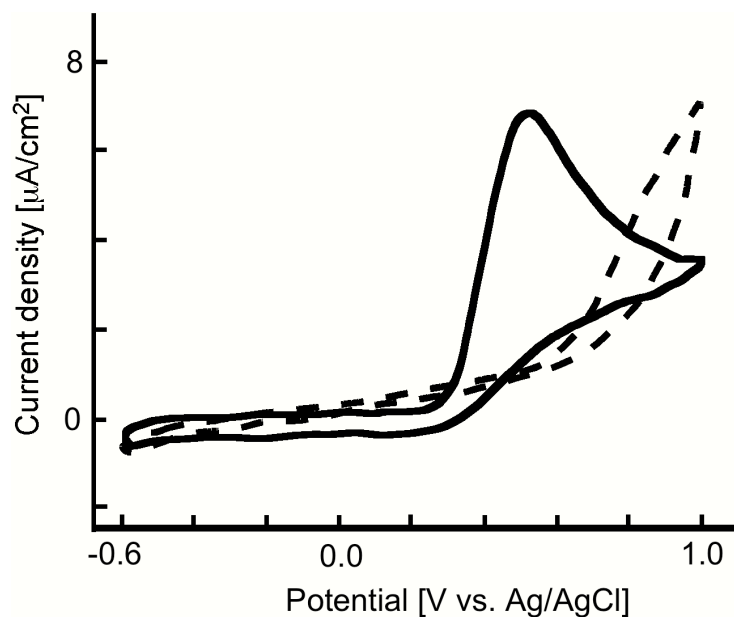


Fig. 3: Cyclic voltammogram of 100 mM uric acid at working electrode of unmodified ITO (solid line) and broken line (PAA-PEI-ITO).

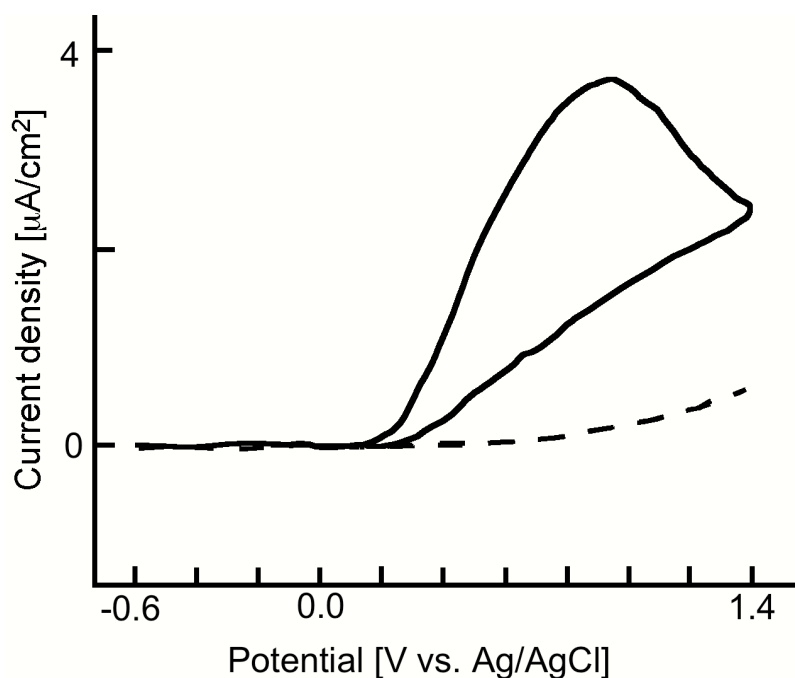


Fig. 4: Cyclic voltammogram of 5.0 mM ascorbic acid at working electrode of unmodified ITO (solid line) and broken line (PAA-PEI-ITO).

### 3.2. Effect of the dye on ECL

The presence of the dye did not affect on the Blank ECL at either of the electrode. However, the S/B ratio at the PAA-PEI ITO electrode was decreased more clearly than that at unmodified electrode was by the dye as shown in **Table 1**.

**Table 1:** Comparison between S/B ratio of Unmodified ITO electrode and that of PAA-PEI-ITO

ITO Electrode	S/B ratio [-]		
	No dye	Eosin yellowish	Beet red
Unmodified	4.97	2.86	4.13
PAA-PEI-	5.57	0.00	1.37

#### 4. DISCUSSION

Both of the dyes used in this experiment hardly adsorb on the unmodified ITO or PAA-PEI-ITO and absorb the light emitted by the ECL reaction very well. Then the dyes mask mainly the photon emitted at the bulk rather than that at the surface of the electrode. Those results suggest that the PAA-PEI layer promotes the ECL by luminol and hydrogen peroxide at the bulk solution. This speculation is supported by the result that blocking anionic reducer by PAA-PEI did not prevent the inhibition of ECL by the reducer.

#### REFERENCES

1. Yoshimi, Y. and Sakai, K. (1993), "Development of a sensitive method for continuous determination of hydrogen peroxide concentration by electrochemiluminescence", *Trans. Inst. Chem. Eng. Part C*, **71**, 279-284.
2. Yoshimi, Y., Kamada, M., Ohkawara, Y., Hattori, K. and Sakai, K. (2004), "Improvement of Hydrogen Peroxide Sensitivity by an Electrochemiluminescent Method with Luminol using Polyion Adsorption onto the Electrode", *Electrochemistry*, **361**, 747-750.