

## Electrogenerated chemiluminescence reaction in Ruthenium-complex/organic-acid system on boron-doped diamond

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### Introduction

Boron-doped diamond thin film has emerged as an attractive electrode material due to its wide electrochemical potential window and low background current in aqueous media. However, as the diamond electrode does not exhibit the electrocatalytic activity, the selectivity for specific compounds is relatively low. Electrochemical sensing method of the electrogenerated chemiluminescence (ECL) reaction using  $\text{Ru}(\text{bpy})_3^{2+}$  can endow the selectivity for the specific compounds to BDD without losing its superior properties.<sup>(1)</sup> On the other hand, it has been reported that BDD electrode can easily discharge hydroxyl radical ( $\text{OH}\cdot$ ) by applying higher anodic potential ( $>2.6\text{V}$  Vs.  $\text{Ag}/\text{AgCl}$ ) in aqueous media. The generation of  $\text{OH}\cdot$  has been confirmed by spin trap method with ESR.  $\text{OH}\cdot$  generation has not been observed at other electrode (glassy carbon, Pt). In this study, we demonstrated the noble ECL reaction in oxygen evolution region ( $>2.6\text{V}$  Vs.  $\text{Ag}/\text{AgCl}$ ) by combining ECL reaction with  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{OH}\cdot$  generation at BDD electrode. Organic acids were used as a co-reactant in ECL system of  $\text{Ru}(\text{bpy})_3^{2+}$ , and the clarification of the mechanism of this ECL process was carried out. Moreover, the contribution of molecular structure of co-reactant to this noble ECL process was inspected.

### Experimental

- (1) The electrochemical measurements were carried out in a single-compartment, three-electrode glass cell with an  $\text{Ag}/\text{AgCl}$  (saturated KCl) reference electrode, platinum gauze counter electrode and BDD electrode working electrode.
- (2) The ECL produced on BDD electrode were recorded with a Photomultiplier tube (PMT, Hamamatsu R928) installed shortest distance from working electrode.
- (3) The ECL signal was real timely measured in cyclic voltammograms using PMT.
- (4) The solutions examined in this study were 0.1M phosphate buffer solutions (PBS) containing  $\text{Ru}(\text{bpy})_3^{2+}$  (=Ru complex) and organic acids.

### Results and discussions

Fig. 1 compares the potential-ECL behavior for ascorbic acid at polycrystalline Pt, GC and BDD electrode. Only at BDD electrode, ECL emission in higher potential regions ( $>2.6\text{V}$ ) could be observed. This ECL was not obtained at polycrystalline Pt and GC electrode. Generally, oxygen which is dissolved in water or generated at electrode surface acts a quencher for excite state  $\text{Ru}(\text{bpy})_3^{2+}$ .<sup>(2)</sup> Because of this, ECL signal was not observed at GC and Polycrystalline Pt, but observed at BDD electrode.

Fig.2 shows potential-ECL curves in 0.1M PBS

containing  $100\ \mu\text{M}$   $\text{Ru}(\text{bpy})_3\text{Cl}_2$  and 30mM ascorbic acid (AA) or 30mM tetrahydrofuran (THF) at BDD electrode. In figure.2, three ECL waves were appeared for both AA and THF in the positive sweep. At each peak potential, the process of the formation of the radicals thorough the oxidation of the co-reactant was thought to be different. The radicals reduce  $\text{Ru}(\text{bpy})_3^{3+}$  to  $\text{Ru}(\text{bpy})_3^{2+*}$ . The First ECL peak was obtained at 1.3 V vs.  $\text{Ag}/\text{AgCl}$ . The ECL process at the first peak can be assigned to the catalytic oxidation of co-reactant by  $\text{Ru}(\text{bpy})_3^{3+}$ . Second ECL peak was observed at 2.5 V vs.  $\text{Ag}/\text{AgCl}$ . The ECL process at the second peak is assigned to the direct co-reactant oxidation at electrode.

The order of the ECL peak intensity in higher potential region ( $>2.6\text{V}$  vs.  $\text{Ag}/\text{AgCl}$ ) for AA and THF differ from that at first and second ECL peaks. Therefore, the mechanism of the ECL at higher potential ( $>2.6\text{V}$ ) was supposed to be different from that in lower potential region. In order to make clear the mechanism of this noble ECL process in higher potential region, we will clarify the relationship between side-products ( $\text{OH}$  radical) in the oxygen evolution reaction and the molecular structure of the co-reactant.

### Reference

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- (2) Yanbing Zu and Allen J. Bard, *Analytical Chemistry*, 72, 3223, (2000)

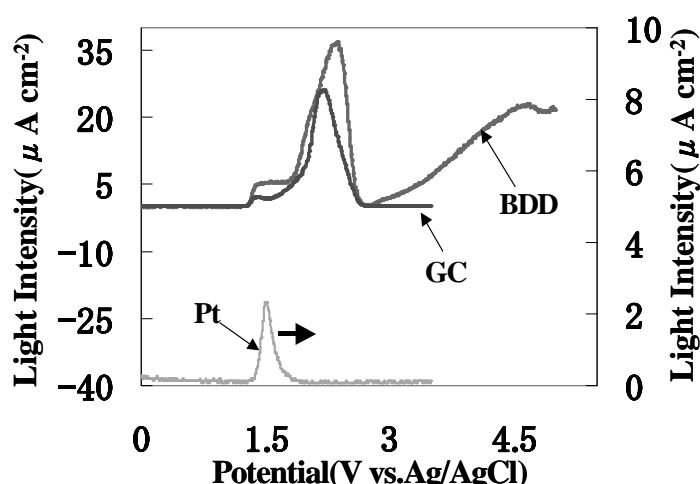


Fig1. Cyclic voltammograms in 0.1M PBS containing  $300\ \mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  and 40mM Ascorbic acid

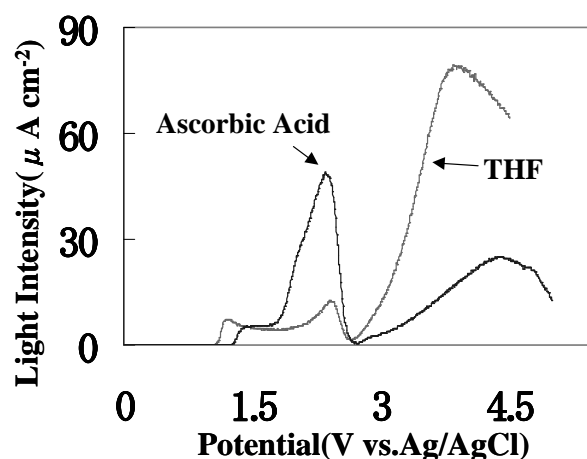


Fig2. Cyclic voltammograms and ECL curves in 0.1M PBS containing  $100\ \mu\text{M}$   $\text{Ru}(\text{bpy})_3^{2+}$  and 30mM AA or THF.