

Simultaneous Electroluminescence

Jorge G. Ibanez,* Daniel Zavala-Araiza and Biaani Sotomayor-MartínezBarranco

Centro Mexicano de Química Verde y Microescala, Depto. de Ing. y Ciencias Químicas, Universidad Iberoamericana – Ciudad de México, Prol. Reforma 880, 01219 Mexico, D.F.

(Received: Sept. 11, 2012; Accepted: Nov. 23, 2012; Published Online: Jan. 20, 2013; DOI: 10.1002/jccs.201200406)

A proof-of-concept for the production of simultaneous electroluminescence in a single electrochemical cell in a basic medium and using H_2O_2 as a co reactant is obtained: at the anode by means of the direct oxidation of luminol to yield an excited emitting species, and in the catholyte by an indirect mediated process involving the initial reduction of ClO_2^- to produce ClO^- , which then reacts with luminol (also to produce an excited emitting species). Emission spectra and possible mechanistic pathways are discussed.

Keywords: Electroluminescence; Paired processes; Simultaneous processes; Luminol.

INTRODUCTION

Modern trends in electrochemical processes include the design of *simultaneous processes* – namely those in which the anodic and cathodic reactions are useful. This avoids the need for a “sacrificial reaction”, which reduces the generation of waste and its concomitant consumption of electricity. In rather exceptional cases, both electrodic reactions yield the same substance (i.e., *convergent simultaneous or paired processes*).^{1,2} For example, the convergent paired production of ClO_2 , an environmentally-friendly alternative to chlorine for water disinfection and treatment and for pulp bleaching, has been reported by us through the simultaneous reduction of ClO_3^- (anodic reaction) and oxidation of ClO_2^- (cathodic reaction) in an electrochemical cell.^{3,4}

In the present work a proof-of-concept is given for a system in which both electrodic reactions can be used to produce electroluminescence, *ECL*. This phenomenon occurs when one of the substances involved in an electrodic reaction arrives at an excited state from which it can emit light upon returning to its ground state.^{5,6}

Luminescence-based analytical techniques can offer considerable sensitivity and selectivity.⁷ Compared to conventional chemiluminescence (CL), ECL is amenable to more precise control and offers greater flexibility.⁷ In addition, ECL does not suffer from common interferences found in electrochemical systems due to the undesired electroactivity of analytes since the ECL measured signal is not electric but radiative.⁸ ECL typically uses $\text{Ru}(\text{bipy})_3^{2+}$ or 2,3-aminophthalohydrazide (luminol) as the emitting species, and offers abundant actual and potential uses in the

fields of: a) bioassays, like immunoassays of human reactive proteins,⁹ determination of biosubstances through the use of oxidases,^{8,10} and bioaffinity studies,¹¹ b) organic substance assays (e.g., amines and uric and ascorbic acid),^{7,10} c) the production of luminescent displays,¹² d) elucidation of reaction mechanisms,⁷ hydroxyl radical production monitoring,¹³ toxicity screens,¹⁴ among others. Co reactants like H_2O_2 ,¹¹ peroxydisulfate,^{11,15} peroxydiphosphate,¹¹ azide ions,¹¹ and EDTA⁷ are often used for enhancing the ECL signals and can be used for the study of the electrochemical oxidation activity of various species.¹⁶ Interestingly, Bard's group has achieved electroluminescence with a single faradaic electrode.¹⁷

A simultaneous ECL process could in principle be used for analysis requiring oxidation or reduction of analytes. To the best of our knowledge this possibility has not been developed to date and thus the purpose of the present work is to demonstrate as a proof-of-concept that such simultaneous ECL is possible. In order to use the simplest possible system, the same luminophore should be used in both sides without the requirements for rigorously purified, deoxygenated, nonaqueous solvents.⁵ To achieve this we selected luminol, which is known to undergo chemical or electrochemical oxidation in basic conditions to yield a relatively long-lived excited state from which it emits blue light.⁵ Luminol is as a good candidate for the present purpose as its anodic oxidation can produce the excited state from where it luminesces and at the same time, the cathodic route could be based on the tunnel emission of hot electrons into an aqueous solution for the production of highly reactive sulfate or hydroxyl radicals at oxide-covered Al sur-

* Corresponding author. E-mail: jorge.ibanez@ibero.mx

faces, as these radicals in turn oxidize luminol to its emitting excited state.¹¹

However, this path involves the application of an alternate current protocol that increases the experimental difficulty. Conversely, the luminescence of luminol produced by its oxidation with ClO^- (in the absence of H_2O_2) has been known for almost a century.¹⁸ Since electrolytically-generated ClO^- also produces this luminescence in the presence of H_2O_2 as a co reactant,¹⁹ this marks a highly desirable alternative route. However, care has to be exercised since hydrogen peroxide deprotonates in an alkaline medium; the resulting HO_2^- can in principle react with ClO^- to yield singlet dioxygen (known to emit at ca. 620 nm), which may interfere with the present purpose; fortunately, this possibility has been experimentally ruled out since there is no emission in the absence of the luminophore.¹⁹ Thus, an obvious strategy to achieve the cathodic contribution to the desired simultaneous ECL would be to attempt its production from the reduction of ClO_2^- to ClO^- in the presence of H_2O_2 , as described below.

EXPERIMENTAL

The proposed individual processes were studied first to better understand each and find the necessary conditions to achieve ECL in both. For this, a conventional three-electrode cell was used and connected to a potentiostat (Bioanalytical Systems, model CW-50) as follows.

Anodic ECL

The single-compartment cell was equipped with a Pt wire (Aldrich, 99.9%, 10 cm long, 0.5 mm diameter) as the working electrode, a graphite rod as the counter electrode (Steadtler Mars HB, 2 mm in diameter), and a Ag/AgCl reference electrode (Bioanalytical Systems, BAS, USA). A 9×10^{-3} M luminol solution (Aldrich, 97%) was prepared in 0.1 M NaOH (Baker Analyzed). 100 μL of 10% H_2O_2 (diluted from 30% H_2O_2 , Baker Analyzed) was added as co reactant to 5 mL of the luminol solution.

Cathodic ECL

A divided cell equipped with a cationic exchange membrane (Nafion 417, Aldrich) was used to prevent any oxidized luminol products from migrating to the catholyte.¹¹ A graphite rod of the same characteristics as above was used as the anode, a Pt gauze was used as the cathode (Aldrich, 1 cm^2 , 99.9%), and an Ag/AgCl electrode was used as the reference (BAS). The anolyte solution consisted of 5 mL of 0.1 M Na_2SO_4 (J. T. Baker, analytical grade). The catholyte was 5 mL of 1 M NaClO_2 (Aldrich, 80%). As the electrochemical reduction was initiated, 2 mL of the

luminol/ H_2O_2 solution described above was added drop wise on top of the Pt gauze to produce the electroluminescence in the cathodic side.

Simultaneous ECL

The same cell was used as in the cathodic ECL process, with the Pt wire as the anode, the Pt gauze as the cathode, and the Ag/AgCl reference electrode (BAS) was used to monitor the cathodic potential. A conventional power source was used (TES-6100 DC variable power supply). The same anolyte as in a) and the catholyte as in b) were used.

For the characterization voltammograms, a Pt minidisk electrode (BAS) was the working electrode, a graphite rod (the same as above) was the counter electrode, and the Ag/AgCl (BAS) was the reference electrode. Light emission was captured from the anodic emission through an optical fiber using a miniature UV-VIS Ocean Optics spectrophotometer (model USB4000, integration time = $2 \times 10^6 \mu\text{s}$, number of pixels = 3648.)

RESULTS AND DISCUSSION

Electrochemical characterization

Since the basic solution of luminol was to be present in both electroodic compartments, linear sweep voltammograms (LSV) were run in the cathodic and anodic directions to determine the potential window in which luminol remained stable. In the anodic LSV (Figure 1) a broad oxidation signal was observed (apparently composed of two waves) from ca. 200 to 800 mV vs. Ag/AgCl. In the cathodic LSV (Figure 2) a broad reduction signal was observed from ca. -100 to -600 mV vs. Ag/AgCl (peak at ca. 450 mV).

In order to characterize the reduction of ClO_2^- as a function of potential, an LSV was run in the cathodic direction (Figure 3). A broad peak at ca. -550 mV was obtained.

ECL production

Anodic ECL

In order to obtain the anodic ECL, an anodic potential

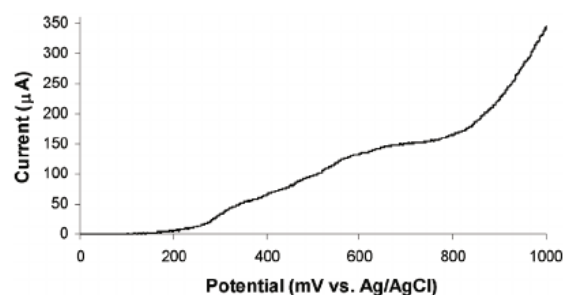


Fig. 1. Anodic LSV for luminol in a basic medium. $v = 500 \text{ mV s}^{-1}$.

of a minimum of 200 mV (and up to the solvent decomposition) was applied to the luminol-H₂O₂ system described above. A blue ECL emission at the Pt electrode was immediately produced (and it remained for several seconds even after turning off the power source).²⁰ The resulting spectrum is shown in Figure 4.

The full mechanism of luminol emission in aqueous non deaerated solutions is complicated as it can be produced by active oxygen species electrogenerated at different applied potentials.^{19,21} Reported ECL peaks in the presence of dioxygen are thought to be due to: a) reaction of luminol radicals with O₂ and their further electrooxidation, b) electrooxidation of OH⁻ to HO₂⁻ and then to O₂⁻ that reacts with luminol, and c) reduction of dissolved oxygen to HO₂⁻ at negative potentials. Under a nitrogen atmosphere an ECL peak is reported at potentials where OH⁻ ions become oxidized to O₂, followed by reaction with luminol.^{19,21}

Cathodic ECL

In order to obtain the cathodic ECL it was necessary to first ensure that the ClO⁻ would produce luminescence upon reaction with luminol under the present experimental conditions and without an applied potential. A strong blue chemiluminescence was indeed obtained upon adding a

few drops of the luminol/H₂O₂ solution to 5 mL of commercial hypochlorite (5% w/w). The same experiment was then repeated using a 1 M NaClO₂ solution instead of the ClO⁻ solution, and no light emission was observed here; this ensured that the sole presence of ClO₂⁻ was not enough to produce ECL by its chemical oxidation of luminol. To reduce ClO₂⁻ to ClO⁻ on the Pt gauze a cathodic potential of -200 mV was applied in the presence of luminol. The cathodic peak in Figure 3 implied the possibility of obtaining ClO⁻ under these conditions. However, no ECL was observed since luminol is most likely reduced to a non emitting species. A different qualitative strategy was then attempted, this time by firstly reducing ClO₂⁻ (setting the Pt gauze cathode at ca. -200 mV), and then adding 1 mL of the basic luminol/H₂O₂ solution to the catholyte.

This procedure was successful as it yielded an intermittent luminescence because luminol reacts with ClO⁻ as this is produced. See Figure 5.

The presence of ClO⁻ provokes the oxidation of the luminophore into an excited state in the catholyte (i.e., a mediated or indirect electrochemical process). A plausible

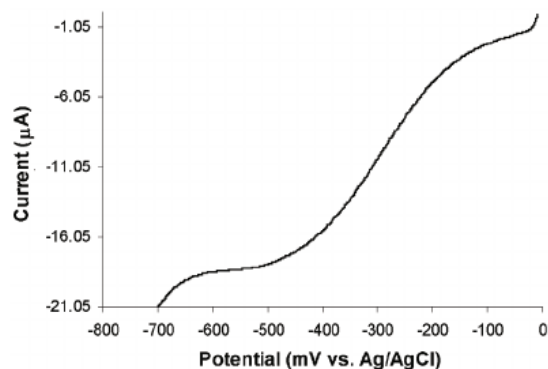


Fig. 2. Cathodic LSV for luminol in a basic medium. $v = 500 \text{ mV s}^{-1}$.

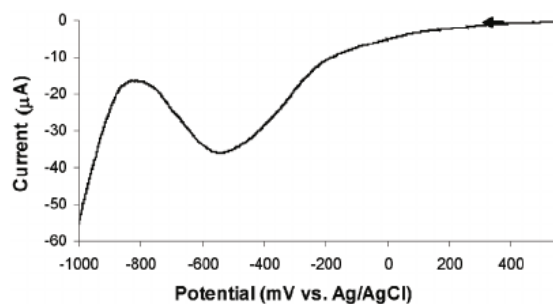


Fig. 3. Cathodic LSV for ClO₂⁻. $v = 200 \text{ mV s}^{-1}$.

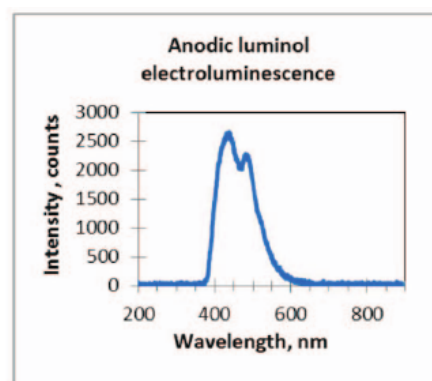


Fig. 4. Anodic luminol electroluminescence. (Experimental conditions are described in the text.)

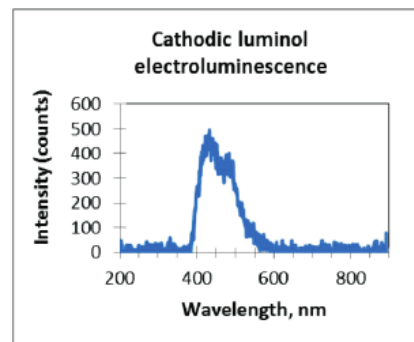


Fig. 5. Cathodic luminol electroluminescence. (Experimental conditions are described in the text.)

18. Rusling, J. *The Electrochem. Soc. Interf.* 2009, *Summer* 34-38.
19. Chi, Y.; Dong, Y.; Guonan, C. *Anal. Chem.* **2007**, *79*, 4521-4528.
20. Liu, C.; Bard, A. *Anal. Chem.* **2005**, *77*, 5339-5343.
21. Sotomayor Martínez-Barranco, B.; Zavala-Araiza, D.; Ibanez, J. G. Book of Lectures, 1st Electrochemical Engineering Students Workshop, 5th. European Summer School on Electrochemical Engineering: Almagro, Spain, September 6-11, 2009; pp 530-537.
22. Ibanez, J. G.; Zavala-Araiza, D.; Sotomayor-MartinezBarranco, B.; Torres-Perez, J.; Camacho-Zuniga, C.; Bohrmann-Linde, C.; Tausch, M. W. *J. Chem. Educ.* **2013**, In press.
23. Bolton, E.; Breyfogle, B.; Gordon, A.; Richter, M. M. *Chem. Educ.* **2007**, *12*, 15-17.

