

A Demonstration of Simultaneous Electrochemiluminescence

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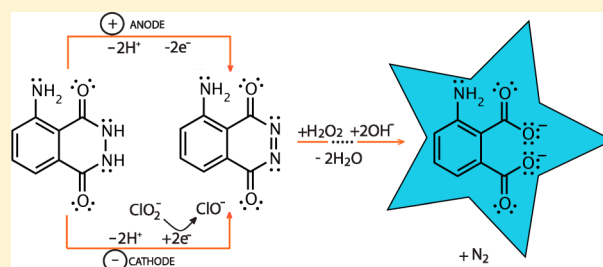
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S Supporting Information

ABSTRACT: Paired (simultaneous) electrochemical processes can increase energy savings in selected cases by using the reactions at both electrodes of an electrochemical cell to perform a desired process, as is the case in the commercially successful chlor-alkali process. In the demonstration described herein, simultaneous blue electrochemiluminescence (ECL) is obtained with luminol in a basic medium in a divided electrochemical cell. ECL is obtained in the anolyte through the direct oxidation of luminol, the reaction products of which interact with H₂O₂ in the vicinity of the electrode to yield an excited emitting species. ECL is also obtained in the catholyte through an indirect, mediated process involving the initial reduction of ClO₂⁻ to ClO⁻, which then reacts with luminol and H₂O₂ to produce the excited emitting species. The co-reactant (H₂O₂) is needed to complete the reaction sequences in both compartments of the cell. This ECL phenomenon is visible to the naked eye in a darkened room at a distance of up to 5 m.

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Modern trends in electrochemical processes focus on the design of *paired (simultaneous) processes*, namely, those in which the anodic and cathodic reactions are both useful. Making both reactions useful avoids the need for a “sacrificial reaction” and reduces the generation of waste and the concomitant consumption of electricity. The best known example is that of the chlor-alkali industry, where a brine solution is electrolyzed to produce mainly chlorine gas (anode) and sodium hydroxide (cathode); these substances are among the top 10 chemicals produced by the chemical industry and are involved in the manufacturing of a wide variety of useful products. In rather uncommon cases, both electrodic reactions yield the same substance (known as *convergent paired processes*).^{1–4} A typical example is the electrochemical production of glyoxalic acid—a chemical widely used as a metal ion reducing agent and in biochemical essays—by the reduction of oxalic acid (at the cathode) and oxidation of glyoxal (at the anode).¹

Herein, a very simple system is described in which both electrochemical reactions can be used to produce electrochemiluminescence (ECL). ECL occurs when one of the substances involved in an electrodic reaction or generated from the product of an electrodic reaction yields a compound in an excited state that emits light upon returning to its ground state.^{5a–c} ECL has actual and potential uses, for example, in bioassays, in luminescent displays, and in experiments to elucidate reaction mechanisms. ECL reactions generally involve

the use of sophisticated luminophores in purified, deoxygenated, nonaqueous solvents.^{6a,b} Such requirements preclude the use of ECL-producing reactions in teaching laboratories. A simple simultaneous ECL system was developed using a single luminophore (luminol or 3-aminophthalhydrazide, Figure 1) in

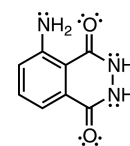


Figure 1. Structure of luminol (H₂L).

both sides of the cell under aqueous (nondeoxygenated) conditions with simple electrodes (e.g., graphite rods) and a readily available power source.⁷ The manual shaking of the electrodes makes this exercise very exciting under low light. This demonstration can be useful for illustrating topics such as redox reactions, electrochemical and photochemical phenomena, and energy conversion, among others in advanced organic chemistry, electrochemistry, and photochemistry courses. Once the reagents have been prepared, the demonstration can be completed in less than 15 min. A discussion of the reactions presented below takes approximately 15–20 min.

DEMONSTRATION DETAILS

A tight cotton plug is used to separate the anodic and cathodic sides of a U-tube electrochemical cell (Figure 2). Depending on

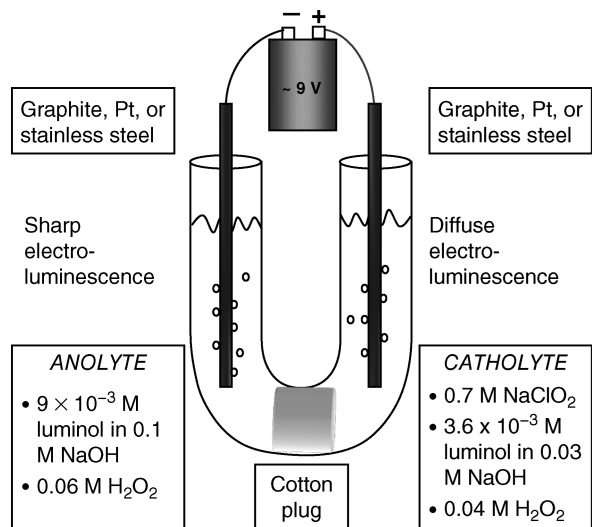


Figure 2. Experimental device. The final concentrations of reagents (i.e., after mixing) are given.

the size of the room used for the demonstration, a large U-tube (for example, a 125 mm-long drying tube with a side arm for visualization from up to 5 m) or a microscale U-cell (for visualization from up to 3 m) can be used.⁸ If available, a video camera can be used in both cases to project images to a large audience. A basic luminol solution (9×10^{-3} M in 0.1 M NaOH) is used as the *anolyte*, to which 100 μ L of 10% H_2O_2 is added for every 5 mL of the luminol solution. A 1.0 M NaClO_2 solution is used as the *catholyte*. Then, another portion of the same luminol/ H_2O_2 basic solution described above is added dropwise to the catholyte (2 mL of this solution are added for every 5 mL of the chlorite solution). Two graphite rods serve as electrodes (for example, Staedtler Mars HB, 2 mm in diameter, obtained at a stationery store) and are connected to an ordinary power source (for example, a battery eliminator) set in the vicinity of 9 V. (If available, Pt electrodes yield more intense electro-luminescence; stainless steel also works well.) If a microscale U-cell is used, a 9 V battery can be used as the power source.

Blue electro-luminescence is observed in the vicinity of the anode, and more diffuse luminescence is observed in the catholyte solution (Figure 3). Shaking the electrodes replenishes the electroactive species for both reactions and sustains the electro-luminescence for a longer period. Light emission can be captured from the steadier anodic emission, for example, through an optical fiber using a miniature UV–vis Ocean Optics spectrophotometer (model USB4000). A spectrum is shown in the Supporting Information.

HAZARDS

Concentrated hydrogen peroxide is highly corrosive to human tissue. Luminol is very irritating to the eyes and skin and is very hazardous if ingested. Sodium chlorite is very hazardous in case of eye contact (irritant), of ingestion, or inhalation and less hazardous in case of skin contact (corrosive, irritant). Prolonged exposure may result in skin burns and ulcerations. Overexposure by inhalation may cause respiratory irritation.

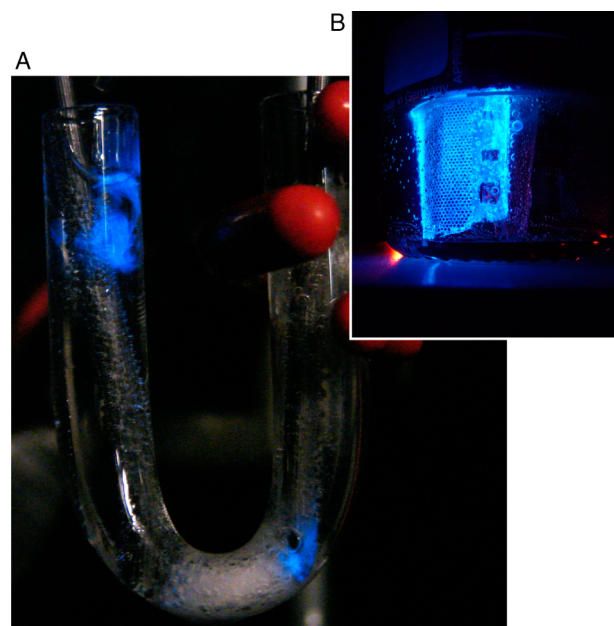


Figure 3. (A) Simultaneous blue electrochemiluminescence of luminol using graphite. (B) Anodic electrode-centric blue electrochemiluminescence of luminol using a Pt electrode from a razor blade.

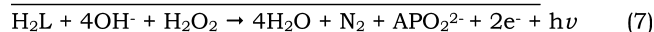
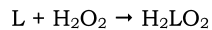
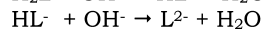
Severe overexposure can result in death. Rubber gloves and eye protection should be used.

RESULTS AND DISCUSSION

The following sequences of chemical reactions conclude with light emission, as discussed below.^{6a,b,7,9–11}

Anodic Electrochemiluminescence

Luminol undergoes electrochemical oxidation under basic conditions to yield a relatively long-lived excited state, which emits blue light.^{5a,b} In the electrochemical cell, a detailed reaction sequence has not been established experimentally; however, a possible anodic reaction sequence involving the oxidation step 3 is as follows:



where H_2L represents luminol (Figure 1), HL^- is the mono-deprotonated species, L^{2-} is the bi-deprotonated species, L is the oxidized and dehydrogenated diazoquinone species (Figure 4A), H_2LO_2 is its protonated endoperoxide species (Figure 4B), and APO_2^{2-} (Figure 4C) and APO_2^{2-*} represent the ground and excited states of 3-aminophthalate, respectively.^{6a,b}

Cathodic Electrochemiluminescence

The complementary cathodic ECL process uses the reduction of ClO_2^- to form ClO^- , which induces the stepwise oxidation of the luminophore to yield its excited state in the catholyte (i.e., a mediated or indirect electrochemical process).⁷ The primary cathodic reaction is as follows:



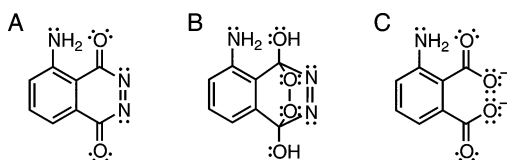
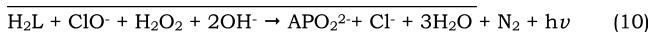
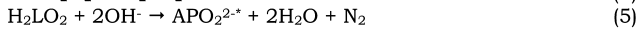
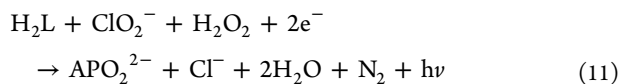


Figure 4. (A) Structure of the diazoquinone, L; (B) the unstable endoperoxide intermediate, H_2LO_2 ; and (C) the 3-aminophthalate ion or 1,2-benzenedicarboxylic acid, 3-amino-, ion (2^-) (APO_2^{2-}).

and the ensuing possible reaction sequence in the catholyte (beginning with luminol oxidation by ClO^-) is as follows:

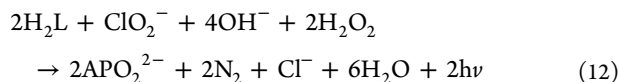


Together with reaction 8 this yields



Overall Cell Reaction

The following overall cell reaction is derived from the previous discussion:



Although not studied here, the presence or generation of dioxygen is known to contribute to the enhancement of ECL at both sides.¹² The overall reaction (eq 12) involves light production in both sides of the cell. Thus, simultaneous anodic and cathodic ECL phenomena are achieved and are visible to the naked eye. The electroluminescence in the catholyte may last for up to 30–40 s, while that in the anodic side may last for up to 3–4 min.

CONCLUSION

A simultaneous electrochemiluminescence phenomenon visible to the naked eye is generated in a basic medium through the anodic oxidation of luminol, followed by a sequence of reaction steps that produce an excited species from which light is emitted. The cathodic process involves the reduction of ClO_2^- to produce ClO^- , which then reacts with luminol to yield the excited species that emits blue light. The co-reactant (H_2O_2) is needed to complete the reaction sequences in both compartments of the cell. The electrical current passing through the cell is thus used on both sides for the same purpose (i.e., light production). Paired processes avoid wasting one-half of the current, which typically occurs in normal electrochemical processes, and can also prevent the production of undesired byproducts resulting from complementary reactions. A case in point is the paired electrosynthesis of cyanoacetic acid (used in several industrial processes and in dye-sensitized solar cells), through the cathodic reduction of CO_2 and the anodic oxidation of a tetraalkylammonium salt anion.¹

ASSOCIATED CONTENT

Supporting Information

Additional information for the instructor. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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