# Analytical applications of electrochemiluminescence: An overview

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# Analytical applications of electrochemiluminescence: an overview

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**Abstract** The chemical transformations of electrogenerated ion-radicals of a number of complex organic compounds may be accompanied by emission of photons. An electrochemiluminescence (ECL) quantum contains information both on the kinetics of the heterogeneous electrode processes and on the subsequent homogeneous chemical reactions in the solution. Application of ECL to solution analysis provides advantages in comparison to electrochemical methods. Using ECL for electrode surface analysis allows information to be obtained on the rate of an electrochemical process simultaneously at all points of the electrode under analysis in real time, and that is the main difference between this method and the point-by-point testing specific to electrochemical methods. The potential of ECL for analytical chemistry is examined concerning the homogeneous ECL-analysis of solutions and the heterogeneous ECL-analysis of electrode surfaces.

## Introduction

Electrolysis of solutions of some complex organic and metallo-organic compounds may be accompanied by light emission from a near-electrode region, i.e. electrogenerated chemiluminescence (ECL) [1–4]. The ECL quanta $\gamma_{ECL}$ are emitted from a singlet-excited molecule ($^1A^*$) which can be produced by electron transfer radicals – a strongly exothermic reaction – from electrically generated anion- ($A^{\bullet-}$) and cation-radicals ($A^{\bullet+}$):

$$A + e \rightarrow A^{\bullet-} \quad (1)$$

$$A - e \rightarrow A^{\bullet+} \quad (2)$$

$$A^{\bullet+} + A^{\bullet-} \rightarrow {}^1A^* + A \quad (3)$$

$${}^1A^* \rightarrow \gamma_{ECL} + A \quad (4)$$

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Reaction (3), being the basis of the ECL process, can compete with various chemical reactions of non-radicals, attack by electrophiles and nucleophiles, interaction with radical-free products, etc. [1, 5–9], although some of the «side» reactions may be accompanied by ECL also. Stage (4) is responsible for forming the ECL spectrum, generally coinciding with the fluorescence spectrum of A.

Chemical interaction of ion-radicals $A^{\bullet+}$ or $A^{\bullet-}$ with appropriate partners (B) present in the solution generally results in the following reaction sequence [1, 10, 11]:

$$B + e \rightarrow B^{\bullet-} \quad (5)$$

$$B^{\bullet-} + E^+ \rightarrow B^{\bullet} + P_1 \quad (6)$$

$$B^{\bullet} + A \rightarrow {}^3A + B \quad (7)$$

$${}^3A + {}^3A \rightarrow {}^1A^* + A \quad (8)$$

Here $E^+$ is an electrophile, $P_1$ is a product of the reaction, $^3A$ is a triplet excited molecule. Stage (8) is a triplet-triplet annihilation, wherein the energy of two interacting particles is summed up. From the above, a diverse number of ECL mechanisms of the considered phenomenon is seen. The mechanism and kinetics of the ECL are defined both by heterogeneous processes on the electrode surfaces and by various homogeneous reactions of electrically generated products. A possible analytical application of the ECL phenomenon is based on the correlation between the processes of the electrochemical transformation of luminophore molecules at the phase boundary (Faradaic current) and the hemiluminescence that accompanies it. By varying both experimental conditions and solution composition a direct proportionality can be reached for the mentioned correlation. ECL analysis enables one to combine the advantages of electrochemical analysis methods (above all, a high selectivity with respect to complex organic compounds) with the very high intrinsic sensitivity of ECL analysis [12, 13].

## ECL – analysis of solutions (homogeneous electrochemiluminescent analysis)

The possibility to use ECL for the analysis of a solution containing LiCl as a background electrolyte was investigated based on the ECL mechanism in solutions. In such electrolytes even those substances which had not produced the ECL effect in solutions with electrolytes such as $Ac_4NClO_4$, gave intensive ECL. Therefore, electrochemical and electrochemiluminescent investigations were carried out on inert electrodes (Pt, Au, graphite, glassy carbon) in different aprotic solvents (dimethylformamide, acetonitrile, propylenecarbonate, etc.) [14] and $Cl^-$ anions were found to be responsible for this phenomenon. Cation-radicals of the organic luminescent products $A^{+\bullet}$ generated at the cathode enter into a fast homogeneous chemical reaction with $Cl^-$ anions and form stable, electrochemically inert free radical products $ACl\cdot$. The reactions form the ECL according to:

$$A + e \rightarrow A^{-\bullet} \quad (9)$$

$$A - e \rightarrow A^{+\bullet} \quad (10)$$

$$A^{+\bullet} + Cl^- \rightarrow ACl^{\bullet} \quad (11)$$

$$ACl^{\bullet} + A^{-\bullet} \rightarrow {}^1A^* + A + Cl^- \quad (12)$$

$$A \rightarrow \gamma + A \quad (13)$$

The homogeneous chemical reaction of $A^{+\bullet}$ with $Cl^-$ competes with the processes of the irreversible destruction of $A^{+\bullet}$ in other chemical reactions. An instability of cation-radicals of the organic luminescence emitting compounds is the main reason for the low intensity or a total absence of the ECL. Rubren and 9,10-diphenylanthracene, the luminescent compounds known for high ECL intensity, produce cation-radicals in dimethylformamide with a lifetime as short as 0.5–2 s. After the interaction with $Cl^-$ it is possible to accumulate a significant amount of $ACl\cdot$ particles in the near electrode region within the anode phase. When transferring to the cathode phase, ECL emitters and initial $Cl^-$ anions arise as a result of an electron transfer reaction between $A^{-\bullet}$ and $ACl\cdot$. A nucleophilic reaction, whereby $Cl^-$ is added to the cation-radicals of complex organic compounds, is, probably, rather abundant as we have observed rise in ECL by several hundred-fold in the investigated organic luminescence emitters of various classes [14].

## ECL – analysis of the surface of electrodes (heterogeneous electrochemiluminescent analysis)

The possibility of applying the ECL method to electrochemical investigation results from the interrelation between the electrochemical interfacial processes (Faradaic current) and the intensity of the ECL. We have performed the ECL investigations of the heterogeneous properties of the surface and Faradaic processes involving some organic depolarizers [15–17]. First, the sample and an electrode (counter) are placed into the ECL cell having at least one surface optically transparent to radiation. Next, the cell is filled with the ECL composition. An electrolysis voltage sufficient for ECL excitation is applied between the sample and the counter electrode. Then, the light image of the surface is examined and registered photographically or photoelectrically and, subsequently, the results are evaluated.

The main problem in heterogeneous ECL analysis is the selection of the electrolysis conditions and the ECL compositions. The latter are the solutions, which are able to transform the electrolysis energy into light. The results of our investigations show that it is necessary to describe the chosen ECL compositions in different ways when studying the surface of the platinum group metals (and also glassy carbon and graphite), semiconductor materials, and metals susceptible to anodic dissolution. When working with such electrodes, one should use special luminescent compositions under cathodic polarization. Similar compositions are necessary for studying the surface of the transition group metals and other metals susceptible to anodic dissolution. For example, the systems studied earlier involved either electrochemically generated polyacene anion radicals and cation radicals of a number of substituted amines formed by electrolytic dissociation [10] or tris(bipyridyl)ruthenium cations and persulfate dianions [18] emitting ECL under cathodic polarization.

Since the resolution of the ECL method of studying the interface is determined largely by the intensity of the radiation emitted during the electrolysis and by the electrolysis conditions, one should use systems possessing a high $I_{ECL}$. Presently, there are a number of compositions emitting ECL of sufficient intensity (up to $10^{12}$ photon/($cm^2$ s)) during electrolysis with rectangular bipolar voltage pulses [15–17]. In our work, we have used a number of compositions possessing a significant ECL intensity within the blue and yellow-red spectral ranges. The compositions were prepared by dissolving polyacenes: 9,10-diphenylanthracene and rubren in the mixture of dimethylformamide-benzene (1:1). The salt $Bu_4NClO_4$ was used as a supporting electrolyte; the adsorption of its cations from the mixture was not observed at the electrodes investigated.

## Results and discussion

ECL – analysis of solutions
(homogeneous electrochemiluminescent analysis)

The revealed effect has been used in the indirect ECL method for establishing the $Cl^-$ anion content in aprotic solvents from the intensity of the ECL organic luminescer-indicator [19]. As an example, Fig. 1 shows a calibration diagram for estimating $Cl^-$ content in dimethylformamide.

All analytical investigations were carried out with the ECL analyzer «ELAN-2», developed by the Electrochemical Laboratory of the Kharkov State Technical University

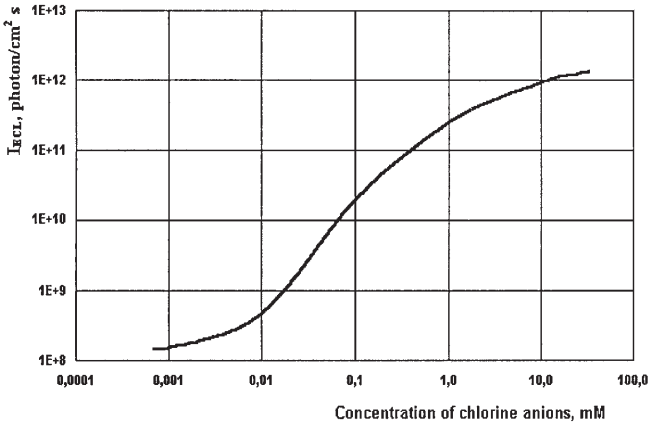


**Fig. 1** Calibrating diagram for $Cl^-$. Electrolyte: 1 mM rubren + 0.1 M $Bu_4NClO_4$ in dimethylformamide. Cathodic ECL on the stationary electrode. Speed of polarization 100 mV/s

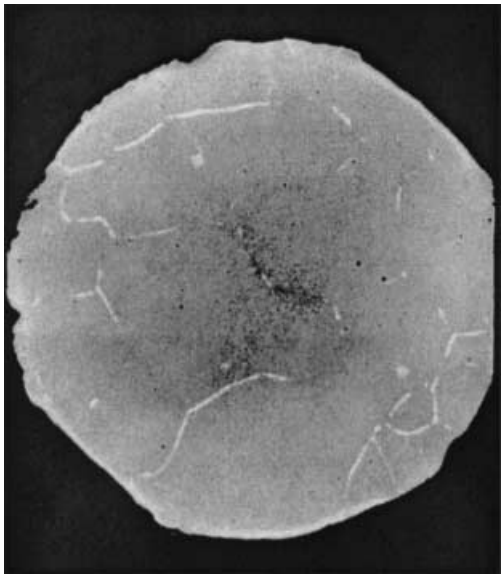

**Fig. 2** ECL image of the platinum polycrystalline electrode. Electrolysis under rectangular bipolar pulses of –3.5 V with a duration of 0.5 ms and an amplitude of 1.35. Electrolyte: 5 mM rubren + 0.1 M $Bu_4NClO_4$ in a volume equivalent mixture of dimethylformamide-benzene (1:1). The diameter of the platinum electrode is 0.5 mm

of RadioElectronics [20]. The highest sensitivity for $Cl^-$ was attained using rubren. 9,10-diphenylanthracene proved a bit less sensitive. Other organic luminophors with less stable cation-radicals led to a sensitivity decrease for $Cl^-$. Probably, in these cases $A^{+\bullet}$ had enough time to decay before encountering $Cl^-$. Decreasing the polarization rate below 100 mV/s should lead to increased sensitivity for $Cl^-$ due to an increase in the reaction time for Eq. (11). However, diffusion then removes the products of reaction (11), $ACl^\bullet$, from the electrode that leads to a decrease in ECL intensity. Probably, it is possible to improve the sensitivity for $Cl^-$ by applying a more complex polarization program, namely, a longer duration for the potential at reaction occurrence and a fast transition to the same duration cathode phase, where measurements of the ECL amount are carried out. Using ECL for the electrode surface analysis allows one to obtain information on the rate of an electrochemical process simultaneously at all points of the electrode under analysis in the real time scale, and that is the main difference between this method and the point-by-point testing specific to electrochemical methods.

## ECL – analysis of the surface of electrodes (heterogeneous electrochemiluminescent analysis)

Figures 2–4 show the photographs of the electrode surfaces of different models obtained during the electrolysis. The ECL intensity distribution over the surface of a polycrystalline rod made of platinum PL-99.9 is shown in Fig. 2. In this case we used a polished face of the rod as a working electrode and observed the grain boundaries at its surface with an average size of 100–150 μm using the microscope under external light. The side surface of the rod has been isolated from the solution by a glass sheath. A platinum counter electrode is placed coaxially to a working one. Note that the ECL intensity increases in the fields between the grains. As the additional investigations have shown, these fields take the shape of a concave wedge. The ECL intensity also increases in some separate areas of the electrode boundary where the microscopic clearances are being formed between the metal and the glass sheath.

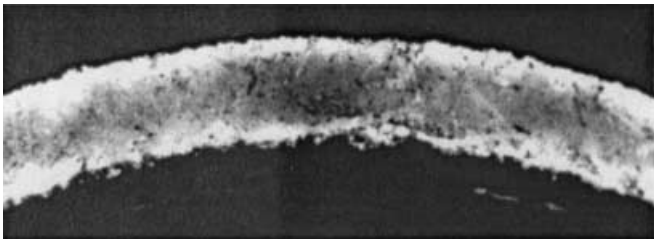

**Fig. 3** Fragment of the ECL image of the platinum ring electrode, 100 μm thick. Pulse electrolysis amplitudes: 3.5 and –4.1 V, duration 0.1 ms. Electrolyte: 5 mM rubren + 0.1 M $Bu_4NClO_4$ in a volume equivalent mixture of dimethylformamide-benzene (1:1)

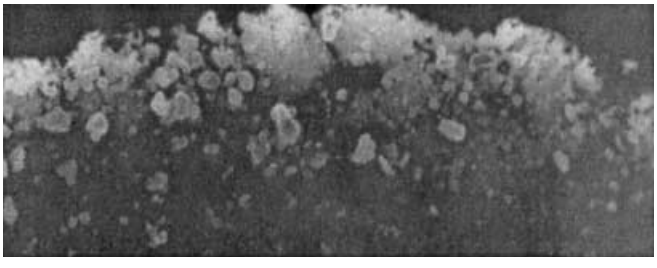

**Fig. 4** Fragment of the ECL image of the graphite disk electrode 2 mm in diameter. Pulse electrolysis and durations: 9.3 V and 0.1 ms (anodic phase) and –10 V and 10 ms (cathodic phase). Electrolyte: 50 mM 1.5-diphenyl-3-styrylpyrazoline + 0.05 M LiCl in dimethylformamide

Another system we have investigated was a rotating ring-disk electrode unit taken from the ELAN-2 complex. In this case, the unit was used as a stationary variant; that is, the disk electrode with a more significant area was the counter electrode and the more narrow ring was the working one. In the ECL image of such a system (Fig. 3) one can clearly see the electrode configuration of the ring, as well as the impurities on its surface. The visible structure of the electrode outside has a developed relief because it draws a fraction of the platinum from the foil forming the electrode during its grinding and polishing. The ECL is not observed in the disk electrode. This fact indicates the absence of the Faradaic processes involving luminescer molecules.

Figure 4 shows the image of the surface of a graphite electrode impregnated with paraffin. One can see the surface heterogeneity, in particular, the electrochemically active areas (bright fields) at which the Faradaic processes that yield ECL emitters occur. Figure 4 presents information about a fraction of the electrochemically active fields at the surface of the electrode, their mean size and distribution versus size, etc.

## Conclusion

ECL can successfully be applied to the analysis of an electrode surface. The method has some advantages: simplicity; ability to study the dynamics of the varying heterogeneity of the whole electrode as well as any of its part during the electrolysis; and the ability to relate the information obtained to the electrochemical activity of the surface rather than to its topography or optical properties.

An important advantage of the method is its high resolution, limited in practice by the ECL wavelength. Notice that the local electrochemically active areas of the surface (e.g., individual punctures of the dielectric film isolating the electrode), which are shorter than the ECL wavelength, can also be observed with the help of the ECL method. It is of interest to estimate the minimal area of the element of the electrode surface, whose irradiation can be detected by a highly sensitive photoelectric multiplier. According to our data the minimal area does not exceed $10^{-12}$ $m^2$ [21]. We have developed a modification to estimate the charging time of the double electrical layer capacity in different sections of the analyzed electrode surfaces [22]. The application of this technique has allowed performance of a metrology control of electric transducers used in the fast electrochemical equipment [23].

The application of ECL to solution analysis has advantages compared to electrochemical methods, since many of those use Faradaic current as the major analytical characteristic. However, it is rather difficult to discriminate this current from an indicating electrode current measurement, and that leads to a limiting determination. Using ECL allows one to register the ECL intensity proportional to the Faradaic current instead of the current itself.

Information on the chemical transformations of the electrogenerated products also provides knowledge of reaction mechanisms and of the solution composition (a number of products of electrochemical reactions are excellent reagents). However, obtaining such information by electrochemical methods is difficult and the further from the surface such reactions occur the more difficult it becomes (slow reactions cause low concentrations of reagents). The ECL occurs as the result of chemical transformations of electrogenerated ion-radicals of luminophors. By gathering photons from the whole bulk one can obtain information on the related ion-radical transformations of the luminophors, which occur at distances far from the electrode, in real time and with very high sensitivity.

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