Redox Chemiluminescence and the Problem of Self-supporting Cold Light Sources

Csaba P. Keszthelyi

The Charles Edward Coates Laboratory, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, U.S.A.

Received June 4, 1975

By generating the redox species at potentials corresponding to the foot of polarographic waves, the conversion of electrical energy into light at efficiencies greater than 100% is shown to be thermodynamically permitted. It is also shown that criteria for this are not met by presently available redox chemiluminescent systems, and the ionquenching efficiency of the electrode is quantitatively evaluated as a function of redox annihilation rate constant, luminescer parent compound concentration, molecular size, and applied potential.

Redox chemiluminescence includes the typical ECL systems where light is produced by radical cation/anion annihilation, as well as other systems where the charge transfer steps are not based exclusively on radical ions. One of the fundamental parameters to be considered in redox chemiluminescence is 

$$\Delta_{v,H} = E_v - |\Delta H_r^0|, \quad \text{where } E_v \text{ is the energy of the emitted photon, and } \Delta H_r^0 \text{ is the chemical energy available from the redox step.}$$

In effect, \( \Delta_{v,H} \) denotes "energy sufficiency," i.e., when the energy of the emitted photon is not larger than the available redox chemical energy, the system is called energy sufficient, and otherwise, energy deficient. Whereas \( \Delta_{v,H} \) is applicable to all redox chemiluminescence systems, in ECL the relationship between \( \Delta H_r^0 \) and \( \Delta E_{appl} \) (the electrical energy expanded), also should be taken into account. The following is a systematic examination of the problem of self-sustaining cool light sources, based on energetic criteria; the results lead to the conclusion that conversion of electrical energy to light at greater than unit efficiency \( (\eta_{ecl} > 1) \) is permitted by the laws of thermodynamics in case of ECL systems.

I. EFFICIENCY OF THE CHARGE TRANSFER STEP

The chemical energy available from the charge transfer step can be calculated as

$$\Delta H_r^0 = \Delta G^0 - T \Delta S^0$$ (1a)

or by referring to the standard oxidation and reduction potentials of \( R^- \) and \( R^+ \),

$$\Delta H_r^0 = E_{O(R,R^-)}^0 - E_{O(R,R^+)}^0 - T \Delta S^0$$ (1b)

* Redox chemiluminescence systems involving non-electrochemically generated reactants are not discussed in the present paper.
and by using 0.1 eV for the last term Eq. 1b can be written at ambient temperatures as

$$\Delta H^\circ_{r0} = \Delta E^* - 0.10 \text{ eV}$$  \hspace{1cm} (1c)

If the first excited singlet of R is the luminescor, then its energy $E_s$ can be compared with $\Delta H^\circ_{r0}$ to decide whether the system is energy sufficient or energy deficient. When $\Delta H^\circ_{r0} > E_s$, the excess energy can not be recovered in terms of photons, hence the conversion efficiency of chemical energy to light is $< 1$. If $\Delta H^\circ_{r0} = E_s$, then unit efficiency is possible, whereas when $\Delta H^\circ_{r0} < E_s$, direct production of excited singlet $^1R^*$ in the redox step itself is generally regarded as energetically unfeasible. In this last case the reaction enthalpy may be sufficient for triplet production ($\Delta H^\circ_{r0} \geq E_t$), allowing intersystem crossing corresponding to E- type delayed fluorescence\textsuperscript{13}

$$^3R^* \rightarrow \rightarrow ^1R^*$$  \hspace{1cm} (2)

Thus an energy deficient system may have $\eta_{c,1} > 1$. Such an occurrence would, however, be severely limited by two practical considerations: (1) the endothermic intersystem crossing represented by Eq. 2 must compete with the exothermic radiationless deactivation

$$^3R^* \rightarrow \rightarrow ^1R_0$$  \hspace{1cm} (3)

and, (2) even for those compounds which satisfy the first condition the usual ECL solution containing a relatively high concentration of (radical) ions will represent a severely quenching environment that compares unfavorably with solutions employed in usual delayed fluorescence studies\textsuperscript{14,15}.

Consequently excited singlet production in an energy deficient system will usually follow triplet-triplet annihilation (TTA), leading to $\eta_{c,1} < 1$.\textsuperscript{a} Some of the ECL systems in which the intermediacy of triplets has been demonstrated involve the anthracene anion with the $N,N,N',N'$-tetramethyl-p-phenylenediamine cation [$$- \Delta H^\circ_{r0} = 2.08 \text{ eV}, E_s = 3.20 \text{ eV}, E_t = 1.8 \text{ eV}$$] and the 2,5-diphenyl-1,3,4-oxadiazole anion with the thianthrene cation [$$- \Delta H^\circ_{r0} = 3.4 \text{ eV}, E_s = 3.6 \text{ eV} \text{ (for PPD)}, \text{ and } E_t = 2.5 \text{ eV} \text{ (for PPD)}$$]. Corroborating evidence for the triplet-triplet annihilation step in ECL had come from quenching of the ECL by known triplet interceptors\textsuperscript{18} and magnetic field effects\textsuperscript{16,17}.

Both energy sufficient and deficient ECL systems are subject to a quantum efficiency that is based on photons emitted per charge transfer event; usually denoted as $\Phi_{c,1}$ (chemiluminescence) or $\Phi_{ECL}$ (in case of electrogenerated chemiluminescence), this parameter in effect appears as a multiplier in the actual energy conversion relationship, i.e. for an energy sufficient system

$$\eta_{c,1} = \Phi_{cl} \left(1 - \frac{\Delta_{r,0}}{\Delta H^\circ_{r0}}\right)$$  \hspace{1cm} (4)

With the exception of the unlikely endothermic intersystem crossing mentioned earlier, the redox chemiluminescence step. e.g.

$$A^- + D^+ \rightarrow A + D + h\nu$$  \hspace{1cm} (5)

converts chemical energy into light at unit efficiency as maximum.

\textsuperscript{a} A possible exception would be tetracene, having $E_t = 1.27 \text{ eV}$ and $E_s = 2.60 \text{ eV}$, hence $2 E_t < E_s$. 
CHEMILUMINESCENCE AND COLD LIGHT SOURCES

Such a restriction does not apply, however, to $\eta_{c,c}$, the efficiency of conversion of electrical to chemical energy. For convenience we may classify the typical cyclic voltammogram of Figure 1 into three zones: 

- $\langle 1 \rangle$, $\Delta E_{\text{appl}} > \Delta H_R^0$;
- $\langle 2 \rangle$, $\Delta E_{\text{appl}} = \Delta H_R^0$;
- $\langle 3 \rangle$, $\Delta E_{\text{appl}} < \Delta H_R^0$.

In all cases the optimum condition $E_s = \Delta H_R^0$, or $\Delta v_s = 0$, may be assumed for a model system, leading to one excited singlet produced per radical ion annihilation. Under these conditions ECL based on electrogeneration of ions in zone $\langle 3 \rangle$ fulfills the prime requirement for a self-supporting cold light source, because the light emitted has more energy than the electrical energy input.

---

**Figure 1.** A typical cyclic voltammogram involving electrogeneration of stable anions ($R^-$) and cations ($R^+$); from such a cyclic voltammogram one usually selects the applied potentials for cyclic double potential steps to be used in electrochemiluminescence. Depending on the relationship between the applied potential difference ($\Delta E_{\text{appl}}$) and enthalpy of the redox reaction ($\Delta H_R^0$), the efficiency of the conversion of electrical to chemical energy varies. Ions electrogenerated past the standard potentials ($E_R^0/R^-$ and $E_R^0/R^+$) are subject to exothermic solvation, while ions electrogenerated below the standard potentials are subject to endothermic solvation, thereby meeting the first criterion of an ideal cold light system. Additional considerations involving the entropy change of the homogeneous charge transfer step are given in the text.

Electrogeneration of ions at the foot of the polarographic wave is commonly known, and for a potential step (3-electrode mode) with boundary condition $C_0(0,t) \neq 0$ the current-potential behavior of a Nernstian system is given by

$$i(t) = \frac{i_d(t)}{1 + \Xi \Theta}$$

where

$$\Xi = \sqrt{\frac{D_o}{D_R}}$$

and

$$\Theta = \exp \left[ \frac{nF}{RT} (E - E^\circ) \right]$$
and \( i_{d(t)} \) is the familiar Contrell equation:

\[
i_{d(t)} = \frac{nFAD_0^{1/2} C_0^*}{\pi^{1/4} t^{1/4}}
\]

(6c)

An ensemble of \( A^- \) or \( D^+ \) electrogenerated in zone \( <3> \) (cf. Figure 1) will be indistinguishable after it accepts libratonal energy from the solvent from an ensemble generated in zone \( <1> \), except that in the first case the solution will cool down, and for zone \( <1> \) it will heat up. Aside from the obvious problem of substantially slowing down the light production process by generating only small amounts of \( A^- \) and \( D^+ \) in zone \( <3> \), an important alteration of the quenching characteristics of the electrodes also occurs in zone \( <3> \), which is discussed in Part II.

II. QUENCHING OF ELECTROGENERATED IONS BY THE ELECTRODE

In order to establish a framework for a discussion of this subject, the results of Christie \(^{19}\) on double potential steps comprise a suitable reference point. He demonstrated that for a stable ion \( R^- \), electrogenerated at the diffusion plateau for time \( t_F \) (= forward pulse time), the immediate application of an oxidizing potential, corresponding to the one electron process \( R^- \rightarrow R^+ + e^- \), for time \( t_B \) such that \( t_B = t_F \), will result in the interception of 58.6\% of the ions. When \( R^- \) is only moderately stable, less than 58.6\% will be intercepted by the electrode under the same conditions, and this has indeed been found to be a useful tool in elucidating not only half-lives but also the mechanisms by which \( R^- \) decomposes\(^{20}\). The well-established method in these studies has been computer (digital) simulation, an approach that has been readily adapted for the electrode condition during \( t_B \) to produce \( R^+ \) rather than \( R^{2+} \). This alternate generation of \( R^+ \) and \( R^- \) (or \( D^+ \) and \( A^- \)) is of course most commonly employed in ECL, hence of special significance to us. Because the ECL boundary conditions follow a monotonic series of cyclic double potential steps, the conclusions derived for the \( N \)th and \((N + 1)\)th pulse, regarding \( \Phi_{ELC} \) and the role of the electrode as quencher of the ionic species, possess general validity. In Figure 2 a schematic simulation of the immediate vicinity of a section of the electrode during the end of the \( N \)th pulse (Figure 2a) and the beginning of the \((N + 1)\)th pulse (Figure 2a, c, d) is shown. Assuming that the \( N \)th pulse was used to generate cations (\( R^+ \)), and it was of a reasonable length to allow the current to decay, indicating a diminishing of the process

\[
R \rightarrow R^+ + e^-;
\]

we find \( R^+ \) surrounding the electrode in essentially uniform concentration. Figure 2b indicates commencement of pulse \((N + 1)\), in which the anion is generated. Following the convention tacitly adopted by the simulation literature, an ideal potentiostat was assumed, capable of establishing the boundary condition.
Figure 2. Quenching of electrogenerated ions by the electrode: schematic simulation of the immediate vicinity of the electrode. (a) at the end of the Nth-pulse most of the R molecules have been converted to $R^+$ in this region of the solution; (b) following the change in boundary condition from $C_{R^+}(0, t) = C_{\text{bulk}}$ to $C_{R^+}(0, t) = C_{\text{bulk}}$, the first layer of $R^+$ was converted to $R^-$ in a two electron reduction step at the commencement of the $(N+1)$th-pulse; (c) the homogeneous charge transfer step between $R^-$ and $R^+$ results in $R^+ + R^-$ (S-route system assumed); (d) fluorescence of $R^+$ and creation of a new layer of $R^-$ at the electrode surface effectively blocks the electrode from any further two-electron reduction of $R^-$ species in the remainder of the $(N+1)$th-pulse. Similar considerations will apply to the two-electron oxidation of $R^-$, indicating that the electrode is not an effective ion quencher. For more detailed considerations including the effect of concentration and size of R, charge transfer rate constant an applied potential, cf. text and Figure 3.

\[
\begin{align*}
C_{R^+}(x=0) &= C_{\text{bulk}} \\
C_{R^+}(x=0) &= 0 \\
C_{R^-}(x=0) &= 0
\end{align*}
\]
electrode at this short distance may well occur to a significant extent. At this point $R$ is again reduced at the electrode to $\hat{R}$, and subsequent diffusion of $\hat{R}$ towards the electrode (Figure 2d) will only supply the cations at a diffusion controlled rate, i.e. the ratio of $\hat{R}$ to $R$ at $x = 0$ will remain $\infty$ for the rest of the pulse, and in effect the «ECL annihilation zone» will sweep out into the diffusion layer, away from the electrode. It is apparent from the aforesaid that within the somewhat ideal context of Figure 2, quenching of electrogenerated ions by the electrode does not take place to a significant extent, the first layer at the electrode surface being negligible compared to the rest of the ions in the diffusion layer for typical concentrations and pulse lengths prevalent in ECL experiments. To gain further insight we may use a quantitative approach to the problem. Assuming that the solute molecules are spherical and 10 Å in diameter, and ionization does not significantly alter this value, the collision cross-section will be $314 \text{ Å}^2$. A microelectrode of 1 mm$^2$ area would require approximately $3.19 \times 10^{11}$ solute molecules to be shielded effectively based on this value of $\sigma$, and the number of moles required ($3.19 \times 10^{11}$ divided by Avogadro's number) is $\sim 5.3 \times 10^{-13}$. Taking 5.3 mM as a representative concentration of ECL parent, the corresponding solution volume is $1.0 \times 10^{-10}$ liters, or $1.0 \times 10^{-4}$ mm$^3$. This requires a $10^{-4}$ mm depth of solution over the working electrode, or 1000 Å, corresponding to 10 monolayers of ECL parent/ion in terms of Figure 2. It should be noted that the depth of coverage required is independent of the electrode area, but is a function of molecular dimension ($r$) and concentration ($M$); Figure 3-a, b, c summarizes these relationships for several values of $r$ and $M$. (The treatment of Figure 3 could have been carried onto an additional dimension by incorporating the half-life of the ions $\hat{R}$ and $R$; as in effect useful ECL systems commonly involve reasonably stable ions, the extended treatment provides little information of value).

The redox reaction rate constant also enters into our consideration, for if only every tenth $\hat{R}/R$ encounter leads to charge transfer, then the required solution depth to shield the electrode will increase tenfold. Slower than diffusion controlled cation/anion annihilation rate constants are predicted if the non-spherical nature of most ECL compounds is recalled, as well as differences in dimer formation depending on relative orientation. In spite of this complication for typical zone $< 1 >$ electrogeneration (applied potential step is to the diffusion plateau region) in millimolar solutions the fraction of electrogenerated ions quenched by the electrode during the opposite half-cycle is negligible, i.e. Eqs. 9a and 9b:

\begin{align*}
\hat{R} &\rightarrow \hat{R}^+ + 2e^-, \quad (9-a) \\
\hat{R}^+ + 2e^- &\rightarrow \hat{R} \quad (9-b)
\end{align*}

represent a negligible fraction of the total current. Essentially the same conclusion has been reached previously by Faulkner, although the research literature also contains an erroneous claim that 17.2% of the electrogenerated ions are destroyed by the Equations 9-a and 9-b (because Eq. 9a, b are 2-electron processes, this would correspond to 34.4% (!) of the Faradaic current).
Figure 3. Quenching of electrogenerated ions at the electrode: 1. the thickness of solution of $R^+$ (or $R^-$) required to effectively shield the electrode from incoming $R^-$ (or $R^+$), as a function of $r$ (molecular dimension), $M$ (concentration), $k$ (homogeneous redox rate constant, expressed in terms of $k_{\text{diff}}$, diffusion controlled limiting $k$).

Legend: (a) $\bullet$: $r = 5 \, \text{Å}$, $k = k_{\text{diff}}$, $C_{R^-}^+ (0, t) = C_{\text{bulk}}$; $\Delta$: $r = 7.5 \, \text{Å}$, $k = k_{\text{diff}}$, $C_{R^-}^+ (0, t) = C_{\text{bulk}}$; $\bigcirc$: $r = 10 \, \text{Å}$, $k = k_{\text{diff}}$, $C_{R^-}^+ (0, t) = C_{\text{bulk}}$; $\bigtriangleup$: $r = 15 \, \text{Å}$, $k = k_{\text{diff}}$, $C_{R^-}^+ (0, t) = C_{\text{bulk}}$; $\blacktriangle$: $r = 20 \, \text{Å}$, $k = k_{\text{diff}}$, $C_{R^-}^+ (0, t) = C_{\text{bulk}}$.

(b) $\bullet$: $r = 5 \, \text{Å}$, $k = 0.1 k_{\text{diff}}$, $C_{R^-}^+ (0, t) = C_{\text{bulk}}$; $\Delta$: $r = 7.5 \, \text{Å}$, $k = 0.1 k_{\text{diff}}$.

(c) $\bullet$: $r = 5 \, \text{Å}$, $k = 0.1 k_{\text{diff}}$, $C_{R^-}^+ (0, t) = C_{\text{bulk}}$; $\Delta$: $r = 7.5 \, \text{Å}$, $k = 0.1 k_{\text{diff}}$.

(d) $\bullet$: $r = 5 \, \text{Å}$, $k = 0.1 k_{\text{diff}}$, $C_{R^-}^+ (0, t) = 0.0001 C_{\text{bulk}}$; $\Delta$: $r = 5 \, \text{Å}$, $k = 0.1 k_{\text{diff}}$, $C_{R^-}^+ (0, t) = 0.0001 C_{\text{bulk}}$.

The inexactness of the assumptions (spherical $R$, $R^+$, $R^-$, neglect of concentration gradient predicted by the error function compliment $\text{erfc} \, z$, infinitely stable $R^+$, $R^-$) diminishes in significance in view of the orders of magnitude differences involved. Necessary pulse length is $\sim \sqrt{\pi \, D}$. 


A significantly different situation arises in zone $< 3 >$ electrogeneration (Figure 3-d); now the applied potential is to the foot of the wave, and the ECL parent concentration ($C_{\text{bulk}}$) no longer provides a reliable estimate of the concentration of ions shielding the electrode. From the Nernst equation it is unmistakable that decreasing the applied potential by 100 mV results in an almost hundred-fold decrease in the concentration of $R^+$ or $R^-$ at $x = 0$ (the electrode surface), and thereby $C_{R^+ (x=0)}$ or $C_{R^- (x=0)}$ may be several orders of magnitude lower than $C_{\text{bulk}}$. Consequently the ion-quenching efficiency of the electrode (Eq. 9a, b), which is generally considered inversely proportional to the concentration of ECL parent ($R$), is more properly related to $[R^+]$ and $[R^-]$ generated. This is particularly important for thin-layer type ECL cells which may be conveniently operated by a DC applied voltage: unless the gap between the thin-layer cell electrodes is of a proper magnitude, very severe ionquenching losses can be expected. For example if the ECL parent ($R$) concentration is 0.5 mM and the cation/anion annihilation rate constant is one half the diffusion controlled maximum, the minimum necessary separation will be 2 microns if Eqs. 9-a and 9-b are to remain negligible in the over-all process, assuming zone $< 1 >$ electrogeneration. On the other hand for the same solution but zone $< 3 >$ electrogeneration at 0.25 V short of $E^0$, the necessary gap between the electrodes would be in the order of 2 centimeters. Hence, zone $< 3 >$ electrogeneration, as well as ECL of trace amounts of $R$, is subject to many special complications.

Even though endothermic solvation of the ions that are zone $< 3 >$ generated allows $\eta_{\text{ECL}} > 1$, no system is presently available to our knowledge with $\phi_{\text{ECL}} > 0.2$ (4,6), therefore should back-conversion of the light to electrical energy be possible at $\eta_{\text{ECL}} = 1$, we are still very far from any practical fascimile of a self-supporting cold light source that would convert ambient heat of the surroundings to light in a continuous manner once started.

One must also take into account a tunneling problem: if $[R] \gg [R^+]$ (or $[R^-]$), the equilibrium for

$$R^+ + R \rightleftharpoons R^+_2$$

is expected to lie far to the right for most actual systems; now for the cation/anion annihilation process we can no longer contend with

$$R^+ + R^- \rightarrow R^* + R,$$

but rather one has to consider

$$R^+_2 + R^- \rightarrow [R_2 \ldots R_2]^\pm$$

The efficiency of electronically excited state production ($R^*$) from the extensive activated complex $[R_2 \ldots R_2]^\pm$ is dubious; even elementary MO theory and configuration interaction correctly predict that the $R^+_2$ (or $R^-_2$) state is expected to be lower lying (i.e. less energetic) than $R^+$ (or $R^-$), consequently $[R_2 \ldots R_2]^\pm$ less energetic than $[R_2 \ldots R]^*$; hence Eq. 12 leads to a tunneling effect whereby the reaction enthalpy $\Delta H^c$ calculated by the usual means no longer represents the actual energy liberated in the redox step. Although it is possible to propose an ideal cold light system where Eq. 10 is altogether negligible, in actual
systems Eq. 12 represents a fundamental obstacle in zone $< 3 >$ electroge-
neration. To mitigate this somewhat pessimistic conclusion, our current system-
matic investigation of $\Phi_{ECL}$ as a function of the $[R]/[R^*]$ and $[R]/[R^-]$ ratio is
anticipated to yield valuable energetic as well as kinetic information on the
dimeric species $R_2^*$ and $R^-_2$, calculated from their change-transfer behaviour.

Acknowledgement. This material was presented in paper No. 295 at the 145th
National Meeting of the Electrochemical Society (U.S.A), May 12—17, 1974, San
Francisco, California; financial support of LSU-SGA is acknowledged.

REFERENCES
94 (1972) 4872.
(1973) 6582.
13. C. A. Parker, »Photoluminescence of Solutions«, Elsevier Publishing Co.,
Amsterdam, 1968, Chapter 2.
94 (1972) 691.
94 (1972) 1522.
6324, 6331; (b) J. T. Bowman, Ph. D. Thesis, The Univ. of Texas at Austin, 1970.
1958.
Chem., 76 (1972) 1868.
Pokazano je da je termodinamički dozvoljena pretvorba električne energije u svjetlo s efikasnošću većom od 100%, ako se stvore redoks vrste kod potencijala koji odgovara podnožju polarografskog vala. Današnji redoks kemiluminescentni sistemi ne pružaju kriterije za ovu pojavu. Ionsko gašenje efikasnosti elektrode je kvantitativno obradeno kao funkcija konstante brzine za redoks nihilaciju, zatim koncentracije ishodne tvari, veličine molekule i primijenjenog potencijala.

THE CHARLES EDWARD COATES LABORATORY
DEPARTMENT OF CHEMISTRY
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISIANA,
USA