Organic electrochemiluminescent displays: degradation and regeneration processes

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Abstract

Construction and basic principals of organic electrochemiluminescent (ECL) displays are briefly described. Light emission degradation processes and known prevention methods are under detailed consideration. At first experimental results of self-regeneration process are presented and possible physical and chemical reasons are discussed. Some analogies with solid state organic light emission diodes are noted.

Keywords: rubrene, electrochemiluminescence, double layer, triplet state, peroxide, degradation mechanism

Introduction

Organic electroluminescence is one of the most perspective novel display technology. But, basic physical and chemical processes as at electrodes so in bulk of organic layers dye not enough experimentally and technologically investigated on present time. Existing theoretical models, which are developed for semiconductor technology or organic chemistry, are not applicable for organic electroluminescence. In such situation investigation of liquid phase recombination type organic electroluminescence (traditionally named "electrochemiluminescence" or "electrogenerated chemiluminescence", which used the same luminophores as organic light emitted diodes (OLED), is being of special interest. Using liquid media and electrochemical processes masks some luminophor properties and evaginates others, open possibilities to better understand all of them.

For example, A.Bard has systematically investigated electrogenerated chemiluminescence of rubrene, which effectively emits light by triplet-triplet annihilation. He also made research of rubrene electrochemical stability in thin electrochemiluminescent cells [1, 2]. Specificated photo-physical and chemical properties of rubrene predetermines its use in novel OLEDs.

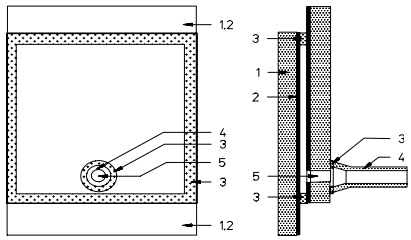
Another material, which is actively used in OLEDs, AluminumQuinolate (Alq3) has rather high electro-chemilumenescence quantum yield (~0.5%) in acetonitrile-benzene solvent [3].

Note, that electrochemical processes in electrochemi-luminescent systems are functionally requisite, but in solid state OLEDs they are parasitic and undesirable. However, the electrochemiluminescence knowledge can be turn to block undesirable electrochemical processes in OLEDs.

Construction, operation and parameters of thin film direct current electrolyteless ECL devices

There are different types of ECL devises, but only thin film direct current electrolyteless ECL devices will be considered in this paper, because their operation is the most similar to OLED's one.

At first such construction was proposed by Phillips corporation in 1982 [4].



1 . Glass plate
2. ITO-layer
3. Ceramic glue
4. Capillary
5. Hole

-light efficiency	***6...8 Lm/W***
-power consumption at 50 Cd/m2	***5 mW/cm2***
-driving voltages	***4...6 V DC***
-response time	***10...30 μs***
-spatial resolution	***25... 50 μm***
-optical transmission	***75...80%***
-operating temperature range	***-55...+50 °C***

Fig 1. Direct current thin film ECL-cell

ECL process is represented at fig 2 - on electrodes from neutral molecules anion and cation radicals are produced, these radicals recombine in bulk of the solution and form the excited molecules, which let out a photon and begin new ECL cycle. Triplet mechanism of radiation is more complicated, but as a whole corresponds to the cycle represented on fig 2.

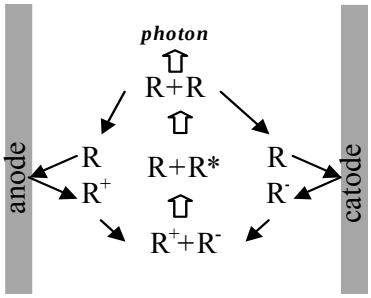
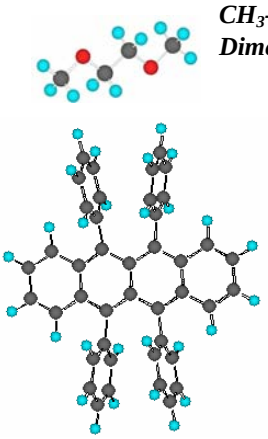


Fig 2. ECL cycle



CH_3-O-CH_2-CH_2-O-CH_3
Dimethoxyethane (glim) ε=7

Rubrene
$C_{42}H_{28}$
(5,6,11,12-tetraphenylnaphthacene)

ES=2.3 eV, ET=1.15 eV
E+=0.87 V, E-=1.53 V
λecl=0.56μ T-way

Fig 3. Solvent and luminofor for the ECL system

Charge transport in electrolyteless ECL cells is very specific. Solution really is dielectric media, but under electrostatic forces electro hydrodynamic instability appears and streams with speed to some meters per second come into existence. Carry of ion-radicals by so high speed streams in 10-50 micron gaps produces current of some mA/cm^2 at 5 V applied bias [5]. Diagram of operation and microphotos of the streams are presented on fig 4.

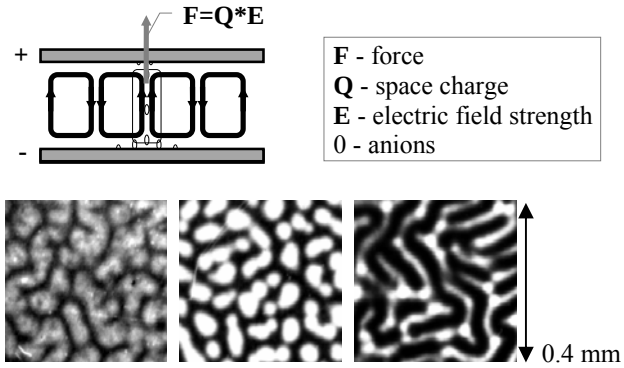


Fig 4. Diagram and microphotos of the streams (for 3 V, 4 V, and 5 V applied bias voltage)

Super thin (with sub micron interelectrode distance) ECL systems had been made by micromechanical methods [6].

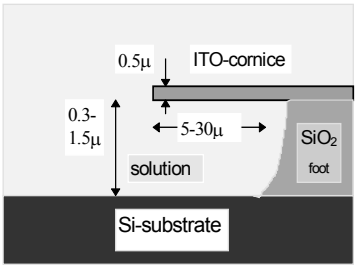


Fig 5. Construction of microfabricated electrochemical cell

Methods of purification the reagents, filling and sealing off the cell are referred on the previous conference [7].

Electrode processes

As noted before, the liquid in the thin film ECL cell is a carefully purified low polar dielectric media. It is seemed unlikely, that amount of ionic impurities in the cell microvolume is enough to form electrical double layers at electrodes. Probably, the electrical double layers are formed from luminophor's molecules or ion-radicals. Measurements of ECL cell discharge kinetics shows that the double layers has anomaly high specific capacity [8]. Note, that conducting polymer PPV also demonstrates high specific capacitance in similar measurements [9].
Results of analyses the data from [8] are presented on fig 6.
If double layer is formed from singly charged ions, their specific weight must be (22/ε) g/cm^3. In high electric fields at double layers ε usually decreases and calculated specific weight is significantly greater than specific weight of rubrene crystal. At present time such questions as "is double layer formed from multicharged rubrene ions, or exist another mechanism for it's anomaly high capacity?" and "are low polar solvent or rubrene molecules directly contacted with electrode in double layer?"are open.

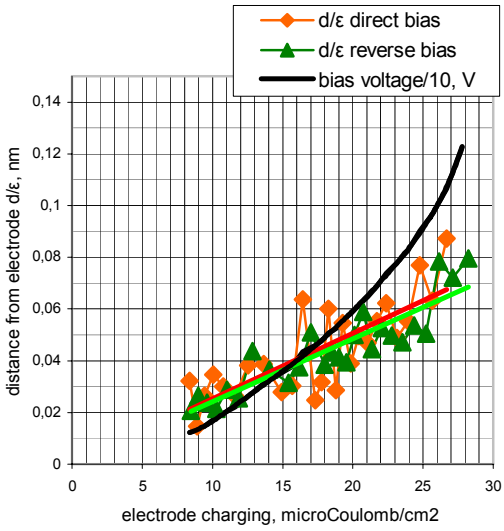


Fig 6. Space charge distribution in the double layer

Electrochemiluminescence of rubrene is realized in T-way: as a result of ion-radical recombination neutral molecule with triplet exited electron is formed. If electrode area is some form of charged rubrene crystal, then lot of specific features must be appeared due to high concentration of triplet exited molecules. Efficiency of triplet energy transfer between aromatic molecules is extremely high, for example

triplet electron changes $10^{11}\ldots10^{12}$ molecules and singlet electron – only $10^{1}\ldots10^{2}$ [10, p.147].
Usually dye crystals don't demonstrated new continuous absorbance bands, which correspond to formation a conductive/valence bands. It means that electrons at normal or singlet levels are not jointed. But the same crystals demonstrate photoconductivity, which can be explained by jointing of triplet levels [11]. Such band is really anomalous: the gap is not indirect, it is "forbidden". May be this is a key for ECL paradox – luminescence appears directly at the anode, but not quenched by the metal electrode.

Rubrene oxidation

Under light exposition rubrene reacts with oxygen and produces the peroxide (see fig 7, left). Light exposition excites dye molecules into triplets, which easier reacts with triplet oxygen molecules. In ECL process, when dye triplets are generated electrochemically, system reactive to oxygen must be extremely high. But peroxide can be effectively regenerated, for example by heating. At 145 ºC the peroxide decomposes into oxygen and rubrene molecules with emission of light [10, p.302].
The naphthacene nuclear is folded, when peroxide is formed, this stoic factor significantly slack as formation so decomposition of the peroxide, because not only oxygen but active vibration excitation are needed for such reactions. On some catalyzers (for example MgI_2) peroxide can irreversible and exothermically transformed into stable oxide (fig 7, right) – another way than antracene peroxide/quinine [12].

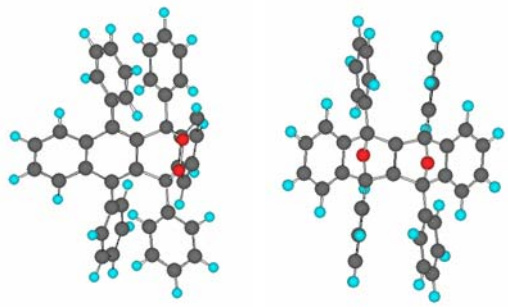


Fig 7. Peroxide and oxide of rubrene

Degradation and self regeneration processes

During operation the ECL cell permanently decolorized, current density and light brightness are decreased. But after sufficient passive period (few weeks) the cell become pinky again, current density and light brightness are restored to previous values. Such cycle can be repeated many times, even for full disappearance of light emission, without visible degradation time after time. It seems to be rubrene peroxide formation/decomposition, but there not enough amaunt of oxygen in the solution. Possible source of oxygen, which is in direct contact with rubrene, is transparent electrode In_2O_3. . Corespondently to chemical potential of the solution, which is different in active and passive periods, stoichiometry of the oxide can change and some amount of oxygen can be eduction or captured. 0,25 μ film of In_2O_3 contains 100 times more amount of oxygen, then it is needed for complete rubrene oxidation, so possible stoichiometric changes is rather small. Note that this surmise is not experimentally checked yet.
If getter is used, it can actively pick oxygen from rubrene peroxide. But oxygen capacity of electrode is commonly higher then getter oxygen capacity, and after saturation the system is working as in absence of getter.

Conclusions

Construction and chemical reactions at thin layer electrolyteless ECL cell are considered. Structure of double layer in electrolyteless ECL systems is analysed. Longevity factors, degradation and self-regeneration processes are discussed..

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