LONG-TIME STABILITY OF ELECTROCHEMILUMINESCENCE ORGANIC LIGHT EMITTING STRUCTURES

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Abstract

Degradation mechanisms of light emitting organic components and factors influencing their long- time stability will be considered. Some methods excluding the adverse factors will be proposed. A possibility of more than 5year operation of such structures will be demonstrated.

Introduction

Special properties of organic substances connected to their complex molecular structure and intermolecular interaction are most clearly shown in liquid phase systems because the ordered structure of solids masks special properties of individual molecules and the large intermolecular distance in gases limits their interaction. Nevertheless, rather encouraging results in solid organic systems were achived by use of superthin (down to monomolecular) layers. In particular, organic light emitting diodes have already reached a competitive level and take their place in the market of display devices. At the same time, investigation of liquid phase electroluminescence has long history, it has solved similar problems and achieved rather good results. In particular, deep investigation of degradation mechanisms, stability and durability of electrochemiluminescence devices has been carried out. In this paper, results for widely used in laser engineering liquid and in and solid electroluminescent systems organic dye 5,6,11,12- tetraphenylnaphthacene (rubrene) are presented. Electrochemilumi-nescence (ECL) systems are poorly known, so their brief description is given in the beginning.

Liquid phase electroluminescence

In liquid phase systems, as well as in solids, two kinds of electroluminescence are possible - field and injection ones. Faraday observed field kind of electroluminescence in organic liquids. The injection electroluminescence in organic liquids was open only in 1964 during electrolyses of organic dye and background salt solutions in aprotonic solvents. The phenomena was named electrochemiluminescence or electrogenerated chemiluminescence. ECL process is represented in Fig.1 - on electrodes from neutral molecules anion and cation radicals are produced, these radicals recombinate in volume of the solution and form excited molecules, which let out a photon and begin a new ECL cycle. Various updatings of this process are possible - so that by alternating current excitation the processes of ion-radicals formation are separated not in space, but in time, accordingly, recombination occurs not in solution volume, but near to an electrode. So triplet mechanism of radiation is more complicated, but as a whole corresponds to the cycle represented in Fig 1.



Fig 1. ECL cycle

Quantum output of ECL with carefully cleared components may reach 20 %. Examples of the substances used in ECL cycle are given in Fig 2.



Fig.2. ECL reagents

When alternating current ECL is carried, it needs complex processes of clearing and work with diverse reagents - molecular dye, ion salt and polar solvent. In such systems, even at the most careful design (see Fig 3), it is practically impossible to get rid of impurity of water, protons and oxygen. Actually, the system degrades after several cycles, but due to a rather big volume of a solution, the life time is enough for realization of scientific research. So, a cell of volume 1cm³ with an electrode of 1 cm in length and 1 mm in width, the dye concentration of 5 mM and the adegradation period of 10 cycles, will work about three hours at the current density of 1 mA/cm². By increasing the solution volume, especially careful clearing and small currents, it is possible to prolong the operating time to 100 hours [1]. It is obvious that such cells are basically of academic interest only.



There were attempts to create the practically preferable thin layer direct current cells with the continuous operating time less than 3 minutes (Tetrabutylammoniumperchlorate, Benzonitrile, Rubrene, 50 microns), and in systems without background salt - about 10 minutes [1]. The analysis carried out in [2] has shown that despite the careful clearing of reagents there is amount of a non- identified impurity with comparable to dye concentration and that the solvent is not electrochemically stable enough at used potentials. After attempts to make extreme deep clearing of reagents, the time of continuous operation increased to about 30 minutes; the use of pumped thin cells has allowed to reveal endproducts of dye degradation - isomers of dihydrorubrene [3]. As a result, the conclusion about practical hopelessness of such ECL cells was made. Therefore, further development of ECL devices is connected to transition to thin electrolyteless cells with low polarity solvent.

Thin layer electrolyteless ECL cells

Low polarity aprotonic solvents are characterized by high chemical and electrochemical stability and are easily cleared of water, oxygen and salt impurity traces. Their use in thin ECL cells allows solving many problems, however, such decision is not obvious at all - in absence of background salt a molecular dye solutions are high-quality dielectrics and at usual potentials should not pass a current. Therefore, reception in system (glim, rubrene, 30-80 microns) [4-5] bright and stable ECL was certain by unexpected. In Fig. 3, the design of a thin ECL cell is schematically shown and a report of its basic characteristics is given.

Subsequently, it was established that conductivity of thin ECL cells appeared due to hydro-dynamic carry of ions – radicals and streams with the speed of some meters per second come into existence in a 20 microns cell [6,7]. Super thin (with a sub-micron interelectrode distance) ECL systems has been made by the micromechanical methods and were investigated [8].



Fig.4. DC ECL-cell

Preliminary purification of reagents

Dimethyl ethylene glycol ether usually contains as impurity methanol (about 0,5 %), monomethyl ethylene glycol ether (about 0,5 %), water (on term and conditions of storage up to 5 %) and the antioxidizers, which interfere formation of peroxides. The antioxidizers may be or N-benzil-n-aminophenol (15 mg per litre), or diethylenetriamine, triethylenetriamine, tetraethylenepentamine (50 mg per litre).

Preliminary clearing of dimethyl ethylene glycol ether is carried out as follows: • the ether was passed through a column with activated aluminium oxide • holded out within day above sodium or potassium hydroxide ◆in dry nitrogen atmosphere overtake in a flask in which it is added potassium ◆in dry nitrogen atmosphere boiled within 10 hours in a flask with fresh potassium under a return refrigerator ◆benzophenone was added to the flask and after occurrence become blue due to ketil complex, the solvent was overtaken in ampoules ◆the ampoules subjected several cycles of freezing and pumping out under vacuum and then were sealed off.

established It was from the chromatographic result that in the sealed ampoules after storing for months, none of listed above impurities was found. However, open ampoules within a day collect an amount of methanol, monomethyl ethylene glycol ether and waters, at least, equal to their initial concentration. Further. the methanol concentration may raise up to 5%. Thus, removal of antioxidizers results in strengthened formation of peroxides and decomposition of a cleared ether.

Preliminary clearing of rubrene is carried out as follows. Rubrene is dissolved in heated xylene and pour out in distilled cooled methanol. The dropped out deposited on dense glass filter under vacuum and washing out by distilled cooled methanol. All operations were carried out in a boxing filled with dry nitrogen, cleared from oxygen and at red light. After drying on the filter, rubrene is placed in ampoules and maintained under vacuum at a temperature about 70°C for 10 hours, then ampoules were sealed off and kept in darkness.

The most widespread impurities collecting at storage dye are atmospheric gases and water. A classical method of clearing of such impurity is vacuum drying with heating till 60-80°C [5]. However, such method of clearing allows to get rid of physically connected impurity only.

At practical work with dyes, it was found that some chemical impurity is collected at storage (ECL cell functioning essentially depends on a storage time of dye). The known chemical analysis methods appeared insufficiently sensitive and have not allowed to identify the specified impurity. So, step-by-step clearing with checking the ECL functioning was carried out. As a result, it was revealed that the impurity is the chemical compound of dye with oxygen. The most probable compounds represent peroxides and quinines.

It is known, that benzene and naphthalene do not form peroxides, but more complex aromatic compounds (since anthracene and its derivatives) are inclined to formation of peroxides, and this process is sharply intensified under action of light. The structural formula of anthracene peroxide is presented below:



Fig. 4. The oxidized forms of aromatic compounds

Reaction of formation of peroxides is convertible, and at heating to certain temperatures, they break up. Temperatures of decomposition of peroxides:

anthracene

120°C

9,10-diphenylanthracene

160°C

naphthacene

120°C

5,6,11,12- tetraphenylnaphthacene (rubrene) 145°C

Quinines may be formed from peroxides, reaction of their formation is irreversible and restoration of dye needs a full cycle of clearing.

Filling and sealing off

Filling is made in vacuum, in the special equipment represented in Fig. 5.

At first, dye is fallen in a cell, it is connected to the vacuum system and warmed at temperature 150°C within 8 hours. Then in a flow of inert gas the flask is filled by dimethyl ethylene glycol ether and potassium with benzophenone is added, the flask is heated up to fusion potassium and formation blue ketil complex. Degassing by three cycles of freezing and pumping out is made. Then distillation of the solvent into ECL cell is carried out by cooling it. After filling the cell, it was sealed out by candle. For bind of oxygen and water, allocated from a glass at sealing, it is necessary to use getter.



Fig.5. Filling system

The best getter is graphite sated by potassium - C_8K . With it time of continuous operation of ECL cell reaches 500 hours, and without it - only 5-50 hours.

During continuous operation, the cell becomes colourless, the current density and ECL brightness are reduced. But after a long passive period (several days), the cell gets pinkish colouring and restores ECL brightness again. The reason of such behavior can be explained by properties of ions – radicals. They are formed during operation of ECL cells, extremely active are cooperated with oxygen and probably may picked it from ambient materials (tin oxide electrodes and glass). In a passive condition, the system comes back to chemical balance and, apparently, the peroxides are spontaneously decomposed.

Conclusions

A construction and chemical reactions in a thin layer electrolyteless ECL cell are considered. A technology of purification the reagents, filling and sealing off the cell is described. Long time stability and reversibility of degradation during continuous operation are noticed.

References

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