Possibility of a laser action under electrochemical excitation in a cell with a multilayer working electrode

D.A. Vasyanovitch, Y.T. Zholudov, N.N. Rozhitskii
Kharkiv National University of Radioelectronics, Chair of Biomedical Electronics, 14, Lenin Av., 61166 Kharkiv, Ukraine
Phone: +380 (57) 702 13 64, E-mail: rzh@kture.kharkov.ua

Abstract. The possibility of laser action at the solution/working electrode interface in an electrochemical cell with modified electrode by multilayer active organic electrochemiluminescer is considered. Physical and mathematical models for processes of excitation energy transfer and light generation for proposed structure are discussed and results of computer simulation are presented.

1. Introduction

The idea of a laser, utilizing the effect of electrogenerated chemiluminescence (ECL), was proposed in the early 1970-s [1–3]. ECL is the light emission from the excited-state dye molecules, created by the electron transfer between electrochemically generated anion- and cation-radicals. It was supposed that in contrast to conventional dye lasers, a laser operating by this principle would not require an additional source for optical pumping a dye into the required excited state, and may offer additional advantages in terms of efficiency, tunability, range of available wavelengths and miniature dimensions. Numerous analytical and experimental investigations revealed some essential difficulties, specifically concerned with low interaction efficiency of generated light and active medium, thus creating difficulties in achieving the population inversion. To overcome difficulties of lasing under electrochemical pumping several methods were proposed [1, 4, 5]. In this paper the structure of laser, consisting of an electrochemical cell with working electrode with working electrode (WE) modified by the thin film of organic electrochemiluminescer molecules, physical and mathematical models of processes on WE surface, leading to population inversion of electronic levels are considered. Hereinafter this laser is referred to as optochemotronic quantum generator (OCQG).

2. OCQG structure

The main part of OCQG is the electrochemical cell with two parallel-sided electrodes – the working one and the auxiliary one (Fig. 1). Interelectrode space is filled with solution of electrochemically active organic molecules. The WE is modified with the layer of immobilized electrochemiluminescer molecules. The continuos wave lasing is supposed to be realized with the film of immobilized electrochemiluminescer (IEC) serving as the active medium. The ion-radicals of dissolved electrochemiluminescer (DEC) are formed at the surface of auxiliary electrode (AE) and then diffuse towards WE after the voltage is applied to the cell. At the same time, the ion-radicals of IEC are created at the WE and then are reacted with the ion-radicals of DEC with the formation of singlet-excited molecules – the emitters. The generated light is spread in the thin film of IEC, containing emitters, parallel to the WE surface. For the resonator mirrors it is supposed to use multilayer dielectric mirrors with the reflection spectra maximum, corresponding to maximum amplification of the active layer.

3. WE structure

For the considered OCQG scheme the WE structure and properties ought to be determined for the lasing possibi-
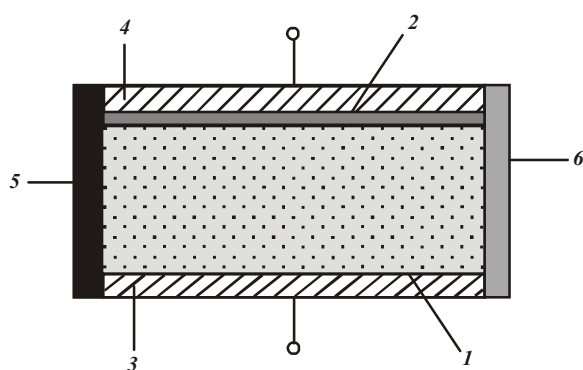
Fig. 1. OCQG structure: *1* – cell with DEC solution; *2* – IEC layer on the WE surface; *3* – AE; *4* – WE; *5* – full reflecting mirror; *6* – partially reflecting mirror.

lity under electrochemical excitation. The main WE functions are:

- effective IEC ion-radicals formation;
- effective transformation of ion-radicals energy into IEC molecules excitation energy;
- effective interaction between emitters and OCQG light wave.

For the purposes of light generation it is necessary to provide minimum losses for absorption, so only transparent to the generated wavelength materials can be used. Many organic semiconductors, either low-molecular crystals or polymers, satisfy this condition. For contact layers thin film of transparent conducting oxides, such as ITO (indium-tin oxide) can be used.

For the effective interaction between light wave and excited active centers it is necessary to provide waveguiding properties of WE by using multilayer structure with the appropriate refractive index profile. The active layer, containing electrochemiluminescer molecules, should serve as a core of this planar optical waveguide. In general this waveguide is asymmetric. The DEC forms one of the waveguide claddings and its refractive index is mostly determined by the solvent optical properties. The second cladding is artificial; its properties should provide maximum waveguiding of WE structure. The active layer should be thick enough to provide stable existence of principal mode.

The excited molecules formation during anions and cations recombination occurs at the solution – WE phase boundary, so in order to provide effective interaction between emitters and OCQG light wave the excitation energy transfer deep into active layer is necessary. The radiative energy transfer can be neglected due to low active layer thickness. The basic ways of nonradiative energy transfer in such multilayer structure are resonance energy-transfer between donor and acceptor molecules of Dexter [4] and Forster [5] types. The Forster energy-transfer process involves a resonant interaction of the transition dipole moments of the donor and acceptor and does not require molecular contact, i.e. it is a through-

space transfer [6]. The Forster mechanism is primarily leads to singlet-singlet energy transfer. Such transfer can occur for donor-acceptor distance over 100 angstroms; its efficiency is determined by donor fluorescence and acceptor absorption spectral overlap, donor quantum yield and lifetime, the relative orientation of the donor and acceptor transition dipole moments. The latter factor leads to enhanced Forster energy-transfer in ordered two-dimensional structures like Langmuir-Blodgett multilayers.

For the considered OCQG structure, it is vital to provide singlet excited molecules formation in the IEC film on the WE surface. Here the determining factors are the ion-radicals charges in the film and solution as well as molecular orbitals energies of recombining ions. The probability of reaction products formation in appropriate energy state is determined by energy sufficiency of corresponding electron-transfer reaction. Besides molecular orbitals energies, the reaction is considerably influenced by products and reactants interaction with their surroundings – the solvent and surrounding IEC molecules. The energy of such interaction differs for reactants and products and also depends on the surroundings. In general, the emitters formation is more probable from cation-radical precursor, so to localize excitation in IEC film, WE should be positively charged, i.e. it should be used as anode of the electrochemical cell and AE should be a cathode.

For the effective cation-radical formation at the WE-solution boundary, the materials used for WE structure formation should posses enough conductivity and should not form barrier junctions in the current flow direction. The formation of cation-radicals in the IEC layer after positive potential application means electron transfer from the highest occupied molecular orbital (HOMO) of IEC molecule to a neighbor organic semiconductor molecule. This can be considered as the hole transfer from the anode contact layer towards IEC layer, so intermediate layers between IEC and anode contact should be hole semiconductors. To provide ohmic contacts to such semiconductors, it is reasonable to use conducting materials with high work function to minimize difference of semiconductor HOMO level and conductor work function. This will decrease potential barrier for the hole injection and thus will lower device operating voltage. It is common to use in optoelectronic devices Au or ITO as anode contacts. The latter is preferred due to its transparency in the visible region and work function tuning capability for enhanced anodic contacts.

In the electrochemical cell with modified WE, the biradical recombination of cations and anions is a heterogeneous reaction (at the electrode surface). The reaction rate of bulky organic molecules is strongly dependent on relative spatial orientation of reactants. Modern methods for thin organic films deposition allows obtaining high-quality monolayers with the strictly controlled spatial molecular orientation in the layer (Langmuir-Blodgett, self-assembly, electrostatic self-assembly and other methods). If one of the reactants is immobilized on

the electrode surface, provided that its reaction centers are directed towards bulk of solution, then the reaction rate will increase considerably compared to a homogeneous reaction in solution.

Another important detail for modified WE is the energy levels structure of molecules, contacting with IEC layer. The IEC excited singlet energy level energy ought to be in contacting layer bandgap for preventing nonradiative intermolecular transfer of IEC excited electron, resulting in emitters quenching and OCQG performance fall. For this reason, IEC can not be deposited directly on metal electrode, because the latter possesses continuous energy spectrum and luminescence on its surface is impossible due to the quenching effect [1].

Summarizing the above mentioned ideas, the WE structure should contain transparent hole-transfer semiconducting layer, doped with IEC molecules, transparent contacts like ITO (Fig. 2). The organic layers can be deposited by means of Langmuir-Blodgett technique or any other.

3. Mathematical model of processes in OCQG WE

For modeling and optimization of WE structure, the following mathematical models development is necessary:

- model of emitters formation and excitation energy transfer deep into IEC active layer;
- model of WE waveguiding structure and principal mode field structure;
- model of coherent OCQG light generation.

Emitters formation rate at the IEC film-solution interface is determined by diffusional anion-radicals transfer in the solution volume and by charge transfer across WE structure with the formation of IEC cation-radicals. In this paper, the conducting properties of multilayer WE structure are not taken into account, so the emitters formation rate is considered to be solely diffusion-limited.
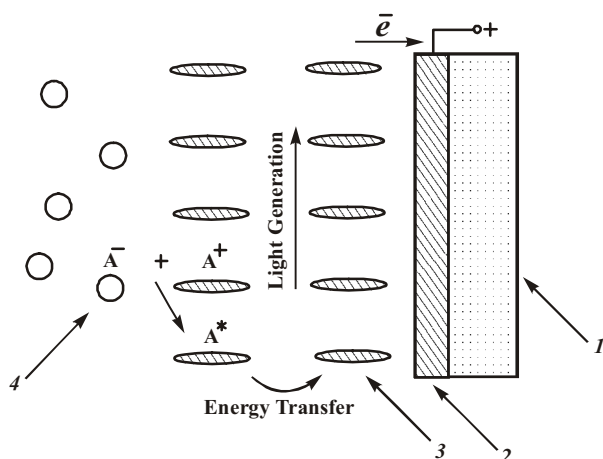

Fig. 2. Physical processes in OCQG WE structure: *1* – substrate; *2* – ITO contact; *3* – IEC multilayer structure; *4* – DEC solution.

The diffusional anions transfer in the electrochemical cell with modiffied WE was quantitatively studied in [8].

The singlet excitation energy transfer between layers of the multilayer Langmuir-Blodgett film is primarily realized via the singlet-singlet Forster mechanism, so the Dexter transfer will not be considered. The Forster theory gives the following transfer rate constant for donor-acceptor molecules:

$$k_F \approx 8.71 \times 10^{23} \frac{k^2 \phi_D}{n^4 \tau_D R^6} \int_0^\infty \frac{f_D(v)\varepsilon_A(v)}{v^4} dv \, , \qquad (1)$$

where k^2 – the relative orientation of the donor and acceptor transition dipole moments (varies from 0 to 4); φ_D – the donor fluorescence quantum yield in the absence of an acceptor; n – the active medium refractive index; τ_D – the donor singlet excited-state lifetime; R – the donor-acceptor center-to-center separation distance; $f_D(v)$ – the spectral distribution of donor fluorescence, normalized to unity; $\varepsilon_A(v)$ – the acceptor molar absorption coefficient; v – the frequency.

In case of multilayer system, the energy transfer from one donor molecule to many molecules of the acceptor layer is possible, so the total transfer rate constant should be calculated. The energy transfer constant is additive. Since the transfer efficiency strongly depends on the donor-acceptor separation, the number of molecules in the acceptor layer that should be accounted in rate constant calculation can be limited. If the Langmuir-Blodgett technique is used to form IEC multilayer structure of electrochemiluminescer and organic semiconductor molecules, then all subsequent monolayers replicate the structure of previous ones. Assuming the uniform distribution of IEC molecules over the monolayer, the following equation for the interlayer energy transfer rate constant can be used:

$$k_{FL}(l) \approx k_0 \sum_{i=-N}^{N} \sum_{j=-N}^{N} \frac{1}{\left((l \cdot \Delta x)^2 + (i \cdot \Delta y)^2 + (j \cdot \Delta z)^2\right)^3}, \quad (2)$$

where $l - 1$ – number of monolayers, separating donor and acceptor layers ($l = 1$ for neighboring monolayers); k_0 – transfer rate constant for unit of donor-acceptor separation distance, calculated using (1); $2N+1$ – number of acceptor layer molecules, accounted in calculation in one dimension; $\Delta y, \Delta z$ – separation distance between two nearest IEC molecules in monolayer in Y and Z directions, assuming monolayer laying in YZ plane; Δx – separation distance between two neighboring IEC monolayers.

Using the equation (2), the rate equations for excited levels population of IEC molecules can be written. The rate equations account two main processes in IEC multilayer structure: resonant excitation energy transfer and spontaneous deactivation of singlet excited levels. The solution of this system allows obtaining stationary emitters distribution across IEC film thickness. The rate equations system contains one equation for each monolayer of IEC film and can be written in the following way:

$$\begin{cases} \dfrac{dN_1(t)}{dt} = \varphi_S \cdot fl(t) - \dfrac{N_1(t)}{\tau_S} + \sum_{j=2}^{m} \big(k_{FL}(j-1)(N_j(t) - N_1(t))\big), \\[4mm] \dfrac{dN_i(t)}{dt}\bigg|_{i=2 \div m} = -\dfrac{N_i(t)}{\tau_S} + \sum_{\substack{j=1, \\ j \neq i}}^{m} \big(k_{FL}(|j-i|)(N_j(t) - N_i(t))\big), \end{cases} \quad (3)$$

$$N_i(0) = 0\big|_{i=1 \div m}, \qquad (4)$$

where N_i – excited singlet levels population of the i-th layer; φ_S – singlet yield of anions and cations biradical recombination; $fl(t)$ – the recombination rate at the film-solution interface, determined by anions diffusional transfer kinetics; τ_S – IEC excited singlet lifetime; m – number of monolayers in IEC film.

For the localization of radiation field in the active layer of WE structure, the formation of planar waveguide structure is considered. So, such structure calculation is necessary to estimate the interaction efficiency between the generated optical wave and excited IEC molecules. The multilayer structure of WE can be limited by five-layers planar structure. For the estimation purpose the exact structure modeling using wave approach is not necessary, the ray approach is quite enough. The calculation of fundamental guided mode structure was done according to method, developed in [9, 10], using matrix approach for optical piles. The calculation was carried out for the following parameters (n – refractive index, d – layer thickness): glass substrate $n = 1.4$; ITO $n = 2.1$, $d = 30$ nm; organic semiconductor layer $n = 1.5$ $d = 50$ nm; IEC doped organic semiconductor layer $n = 1.6$ $d = 100$ nm; DEC solution $n = 1.45$.

Fig. 3 shows fundamental guided mode intensity (1) and refractive index profile (2) of considered structure. The estimated optical confinement factors are $\Gamma = 49\%$ for active organic layer and $\Gamma = 4\%$ for ITO contact layer.

The dynamics of light generation in OCQG is estimated using rate equations system for basic energy levels of IEC molecules involved in laser action. The electronic energy levels of organic dyes consists of broad bands of narrow vibrational and rotational lines and the population inversion is realized between lower vibrational 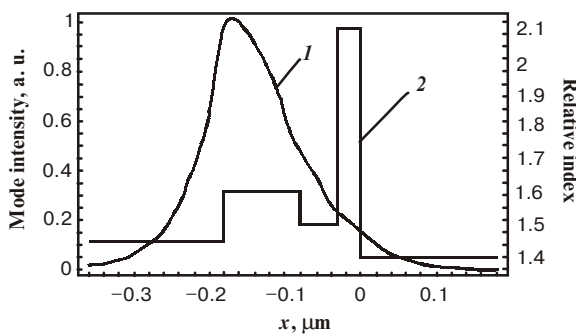sublevels of exited singlet state and upper sublevels of the ground state. This can be mathematically described by splitting the broad ground level into two sublevels with the lifetime of the upper one ("excited ground") equal to the mean relaxation time between vibrational sublevels of the ground state. One of the main features of electrochemical pumping is the high probability of the triplet states formation compared to optical excitation. As the triplets lifetime is higher than the singlets one, its influence over kinetics in the system can not be neglected. The detailed studies of the triplet state influence requires consideration of the Dexter triplet energy transfer mechanism between film monolayers and triplet-triplet annihilation, leading to excited singlet state formation. For this moment, we do not have enough information about above mentioned processes in Langmuir-Blodgett multilayers and in this paper they will be neglected.

The process of stimulated emission is described by photon flux density equation, averaged over the resonator length; the distribution of exited centers is also averaged over the thickness of the film [11]. Such simplified model makes it impossible to predict the beam structure and some other OCQG features, but gives us enough information to determine possibility of laser action, estimate kinetic and energy parameters of the considered device.

The rate equations system for OCQG light generation with initial conditions can be written in the following way:

$$\begin{cases} \dfrac{dN_g}{dt} = -\dfrac{fl(t)}{h} + \dfrac{N_T}{\tau_T} + \dfrac{N_g^*}{\tau_g^*}, \\[3mm] \dfrac{dN_T}{dt} = (1-\phi_S) \cdot \dfrac{fl(t)}{h} - \dfrac{N_T}{\tau_T} + k_{ST} N_S, \\[3mm] \dfrac{dN_S}{dt} = \phi_S \cdot \dfrac{fl(t)}{h} - \left(\dfrac{1}{\tau_S} + k_{ST}\right) N_S - \sigma_S \gamma v I (N_S - N_g^*), \\[3mm] \dfrac{dN_g^*}{dt} = \sigma_S \gamma v I (N_S - N_g^*) + \dfrac{N_S}{\tau_S} - \dfrac{N_g^*}{\tau_g^*}, \\[3mm] \dfrac{dI}{dt} = \sigma_S \gamma v I (N_S - N_g^*) + \Omega \dfrac{N_S}{\tau_S} - \left(\beta + \dfrac{1}{2Lz}\ln\left(\dfrac{1}{r}\right)\right) v I, \end{cases} \quad (5)$$

$$\begin{cases} N_T(0) = N_S(0) = N_g^*(0) = 0, \\[2mm] N_g(0) = N_0, \end{cases} \qquad (6)$$

where N_S, N_T, N_g, $N_g{}^*$ – concentration of singlet, triplet, ground and "excited ground" states accordingly; N_0 – initial concentration of IEC molecules in the film; I – photon density flux; τ_S, τ_T, $\tau_g{}^*$ – singlet, triplet and "excited ground" levels lifetimes; σ_S – singlet absorption cross-section; Lz – optical resonator length; r – partially reflecting mirror reflectivity; v – light velocity in the active layer; Ω – part of spontaneous radiation, amplified by the structure; β – active losses in planar waveguide (mainly due to ITO absorption); γ – coefficient of interaction efficiency between optical wave and emitters; h –
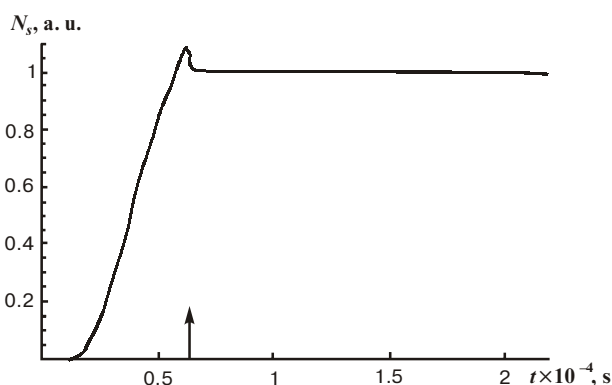

Fig. 3. The OCQG guided mode structure (1) and WE refractive index profile (2).

Fig. 4. Excited singlet states kinetics in OCQG (arrow indicates generation threshold).
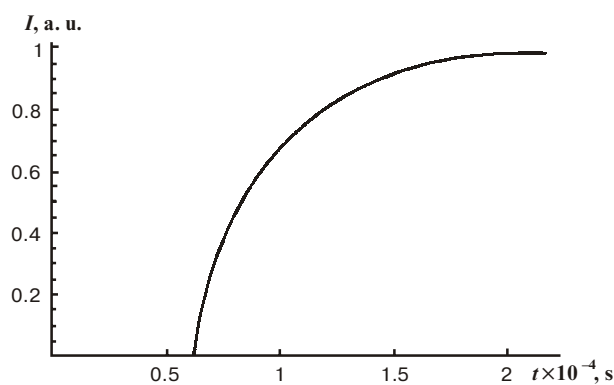

Fig. 5. Photon density flux kinetics in OCQG.

active layer thickness; k_{ST} – singlet-triplet intramolecular conversion rate constant.

The interaction efficiency coefficient γ can be written as a product of two coefficients: the optical confinement factor Γ and interaction factor Ψ, determined from the following equalities:

$$\Gamma = \int_{d_1}^{d_2} I(x)\,dx \left/ \int_{-\infty}^{\infty} I(x)\,dx \right. , \qquad (7)$$

$$\Psi = (d_2 - d_1)\int_{d_1}^{d_2} \langle I(x)\rangle \cdot \langle Nst(x)\rangle\,dx , \qquad (8)$$

where d_1, d_2 – active layer bounds ($d_2 - d_1 = h$); $<I(x)>$ – normalized to unity radiation intensity across active layer thickness; $<Nst(x)>$ – normalized to unity excitation energy distribution across the active layer thickness.

The computation of the given model gives the excited singlet states and photon density flux kinetics in the proposed structure (Figs 4 and 5, accordingly). The obtained results allows estimating whether the coherent light generation in the considered system of OCQG WE is possible. The computation of the light generation model and excitation energy transfer was done for WE modified with 9,10-diphenylanthracene as IEC for IEC/organic semiconductor concentration ratio of 0.1. Further work is necessary to determine triplet states influence on lasing, optimization of IEC and DEC choice, planar waveguide structure optimization, charge transfer rate through multilayer electrode structure estimation.

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