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Simulation of processes in optochemotronic emitter with electrodes modified by Langmuir-Blodgett technique

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The light generation possibility in an optochemotronic device of liquid phase optoelectronics with the working electrode modified by means of Langmuir-Blodgett technique for thin-film deposition has been studied using mathematical simulation. The kinetics of the emitting centers and photons flux density have been calculated for so configured optochemotronic emitter with 9,10-diphenylanthracene as the working electrochemiluminophor being in the film and in the bulk of solution. The possibility to obtain the inversion of electronic level population in the organic luminophor molecules and laser generation under non-optical electrochemical excitation in the optochemotronic emitter has been shown.

Методом математического моделирования изучена возможность генерации света в оптохемотронном устройстве жидкофазной оптоэлектроники с рабочим электродом, модифицированным по технологии Ленгмюра-Блоджетт нанесения тонких пленок. Рассчитана кинетика излучательных центров и плотность потока фотонов для подобной конфигурации когерентного оптохемотронного излучателя с 9,10-дифенилантраценом в качестве рабочего электрохемилюминофора, находящегося в пленке и в растворе. Показана возможность получения инверсной населенности электронных уровней молекул органических люминофоров и лазерной генерации при неоптическом электрохимическом возбуждении в оптохемотронном излучателе.

Optochemotronics denotes the liquid-phase optoelectronics branch that investigates and utilises the luminescence excited non-optically by electrochemical processes in solutions of organic luminophors. The essence of such excitation of electrochemical luminescence (ECL) consists in sequential formation of anion- and cation-radicals of organic luminophor on the optochemotronic emitter (OCE) electrode surface during electrolysis, with subsequent biradical recombination and formation of emitters — molecules in electron-excited state [1]. Among various applications of OCE are liquid-phase light emitting devices, analysis of liquids, information processing, etc. [1]. The possibility to attain the lasing effect in those devices is especially attractive. This problem was theoretically considered in literature at the early 70-s of the last century, however, no certain answer was then obtained [1–3]. At present, there are confirmations of such device realization [4], i.e. coherent OCE, however, there are still exist gaps in understanding of physical, chemical, and technological aspects of this problem, design of the appropriate models and emitters themselves.

The work is devoted to diffusion transfer and radiative processes study in OCE with working electrode modified by Langmuir-Blodgett (LB) technique [5] in pre-threshold mode by means of simulation. The OCE electrode modification using above mentioned technique has some peculiarities and positive features [6]. At the same time, it is to emphasise that this approach was never considered before for coherent OCE and, in out-

look, for OC quantum generator. This also confirms the topicality of the offered approach and investigations carried out in the work.

The coherent OCE model under consideration represents a planar ECL cell confined with two flat electrodes in one direction and two-mirror reflective system in another direction normal to the first one. The linear dimensions of cell electrodes exceed the interelectrode space considerably and the cell can be considered as a thin-layer one. The interelectrode volume is filled with solution of active agent-electrochemiluminophor. The calculations were carried out for 9,10-diphenylanthracene (DPA) that is among the promising luminophors. Anode is chosen to be the working electrode and the emitter formation processes take place on its modified surface. The anode surface is coated by thin electrochemiluminophor film by means of LB technique. The film may consist of either the same luminophor, dissolved in the cell volume, or any other. (In the latter case, so-called "mixed" ECL mechanism involving formation of ion-radical reagents from different precursors can be realized). The chosen film deposition technique allows to control strictly the film thickness and spatial molecular orientation therein. The reagent molecular orientation control during biradical recombination is important for reaction rate rise, because it increases the so called pre-exponential orientation factor in the expression for recombination rate constant [1]. The fixing of reagent molecules with their reacting centers oriented towards the cell volume filled with electrochemilumonophor solution is the most preferable one. The chosen luminophor molecules does not possess amphiphilic properties typical for LB technique, and their chemical modification can be necessary to attain a reliable electrode coating.

The physical model of processes in the device under consideration includes the following stages:

— the luminophor anion-radical (AR) formation in the course of Faraday electron transfer from electrode surface after the reduction potential is applied to the cell cathode;

— the immobilized luminophor molecules oxidation and its cation-radicals (CR) formation at the cell anode simultaneously with AR formation at the cathode;

— transfer of the luminophor AR from the cathode into the cell volume towards anode due to electrostatic interaction and diffusion;

— biradical recombination between electrochemiluminophor AR and CR at the anode surface resulting in formation of ground and excited state molecules (the latter can be singlet and triplet excited molecules. Unlike optical excitation, in the electrochemical excitation mechanism, the probability of excited triplet state formation is high [1]. For energy considerations, the excitation energy localization at the preceding CR molecules immobilized in the film is the most probable at the electron transfer reaction. At the same time, AR are oxidized and turn to ground state and diffuse back to cathode);

— radiative and nonradiative deactivation processes of luminophor molecules in electron-excited state generated in the LB layer;

— formation of inverse population of luminophor molecules singlet energy levels in the film and subsequent light generation.

It is to note that, depending on the deposition method of LB layers, the film structure and thickness, additional processes may arise that are to be considered (nonradiative Forster excitation energy transfer [7], tunnel electron transfer, excimer formation, luminescence quenching, etc.). A special attention should be paid for electron transfer possibility from excited singlet level of luminophor molecule to energy levels of metallic electrode possessing continuous spectra, that results in luminescence quenching [1]. To prevent this process, a through selection of working electrode material possessing appropriate energy levels configuration is necessary. In our case, the cell anode is supposed to be made of *p*-type semiconductor with such configuration of energy bands that the luminophor excited singlet state energy would fall into semiconductor electrode bandgap, thus avoiding the quenching. For good-quality deposition of DPA layers by means of LB technique, the electrode surface modification by coating with ordered monolayer of fatty acid or its salt can be used. In this case, a correct account for electrolysis current through monolayer that has tunneling nature is of importance [8].

It is important to notice that presence of wide bands of vibrational-rotational substructure of the luminophor molecule electron levels and account for intramolecular electron transition rules leads to four-level OCE generation scheme. As a rule, the four-

level scheme has low threshold pump power and is easy to achieve population inversion of working levels. For organic luminophors with wide electron levels, this means that the complete inversion of electron levels is not necessary to obtain positive gain in the active medium. To start generation, it is enough to provide only partial inversion of working vibrational-rotational sublevels of excited and ground singlet states in the luminophor molecule.

The appropriate choice of working electrochemiluminophor is also necessary for successful solution of the problem; in our case, we use DPA with luminescence peak about 430 nm. This luminophor has a high luminescence quantum yield in different solvents amounting about 0.9 to 1, according to different sources [9]. The yield of singlet-excited molecules in the biradical recombination process for DPA is also one of the highest among known electrochemiluminophors and reaches 20 % [10]. Unlike most other anthracene derivatives, 9,10-DPA almost never forms excimers and dimers due to its nonplanar molecular configuration, that makes in possible to prevent some side routes of excitation energy transformation competing with the main one considered above [11]. This, for example, allows to use high luminophor concentrations in solution, limited only by its solubility in the solvent used. This fact, as well as a relatively high AR lifetime in solution (about 0.1 to 10 s) provide efficient transfer of electron donors (AR) from cathode to anode in the device. The DPA luminescence quantum yield is also persistent enough against quenching with oxygen present in solution [11].

The processes concerned with light generation in the system under consideration were investigated by means of mathematical simulation. To simulate processes in the cell, it is reasonable to subdivide the problem into two: i) simulation of AR generation, loss, and diffusion processes in the solution bulk and ii) simulation of processes in the luminophor film where CR and electron-excited centers generated in biradical recombination are localized. Processes of the first task are described by the 2nd Fick law modified equation for one-dimensional diffusion with appropriate initial and boundary conditions [1]. The mass transfer process in OCE is considered to be solely diffusion, taking into account the fact that almost all voltage applied to cell electrodes drops across the double layer (DL) at the electrode-solution interface and electrostatic force in the bulk solution is negligible. In the OCE model on the base of thin-layer cell being considered, we can assume diffusion process to be one-dimensional, because AR concentration gradient tangential to electrodes surface is negligible.

The luminophor electrolysis kinetics in thin-layer cell is considerably influenced by interelectrode capacitance due to DL. The finiteness of capacitance charging time can be accounted for in boundary conditions by a term describing exponential voltage build-up $1 - \exp(-t/\tau)$ with time constant τ, depending on the DL capacitance. The latter is important only if the cell capacitance charging time τ is comparable with AR concentration diffusive stabilization time at the cathode-solution interface. For thin-layer cell, the AR diffusion time from cathode to anode is much less than their lifetime, and AR loss account in our case is not obligatory; nevertheless, this process is taken into account in our model for better correctness.

Typically, the heterogeneous reaction rate during organic luminophor electrolysis is high enough to assume AR concentration at cathode-solution interface almost immediately reaching the luminophor concentration in solution volume, c_0. At the same time, the latter is not valid for the anode modified with ordered luminophor molecules film on a dielectric subphase layer. This supposes that the tunneling charge transfer mechanism from electrode to film is possible. In any case, the account for finite heterogeneous reaction rate constant of electron transfer on cell electrodes is one of the distinguishing features of the model being described, that provides obtaining more adequate physical and mathematical device model and corresponding results that are also valid in case of mixed charge and diffusion controlled kinetics.

Taking into account the above-stated, the following equations (1), initial (2) and Neumann boundary conditions (3, 4) [12, 13] can be written for AR diffusion in the cell volume ($x = 0$ — cathode, $x = L$ — anode):

$$\begin{cases} \dfrac{\partial c_g}{\partial t} = D\dfrac{\partial c_g}{\partial x^2} + \dfrac{c^-}{\tau^-}, \\ \dfrac{\partial c^-}{\partial t} = D\dfrac{\partial c^-}{\partial x^2} - \dfrac{c^-}{\tau^-}, \end{cases} \quad (1)$$

$$\begin{cases} c^- = 0, \\ c_g = c_0, \end{cases} \Bigg| \, t = 0 \quad (2)$$

$$\left\{\begin{array}{l} D\dfrac{\partial c_g}{\partial x} = k_c(1 - \exp(-\dfrac{t}{\tau})) \cdot c_g, \\ c^- = c_0 - c_g, \end{array}\right| x = 0 \qquad (3)$$

$$\left\{\begin{array}{l} D\dfrac{\partial c^-}{\partial x} = -k_A \cdot c^- \\ c_g = c_0 - c^-, \end{array}\right| x = \mathrm{L}, \qquad (4)$$

where τ^- is the AR lifetime in solution; $D_g \approx D^- = D$, diffusion coefficients of the luminophor molecules in ground state and AR, respectively; c_g, c^-, concentrations of ground state and AR in solution, respectively; k_A, k_C, heterogeneous reaction rate constants with anode and cathode, respectively.

The solution of the system under consideration makes it possible to find AR concentration and flux at the anode surface ($x = L$) which determine the emitting centers formation and deactivation kinetics in the luminophor film. These processes can be described by rate equations system for main 9,10-DPA energy levels involved in the stimulated emission process. That is the second task of OCE processes simulation. As mentioned above, electron energy levels in organic luminophors, such as 9,10-DPA, are a broad band of vibrational and rotational lines and population inversion is realized between lower vibrational sublevels of the excited singlet state and upper sublevels of the ground one. For convenience of mathematical description, this can be represented as subdivision of the electron ground state band into two sublevels. The lifetime of the higher sublevel ("excited ground") can be taken equal to relaxation time within ground state vibrational sublevels. Since electrochemical pumping provides a high probability of triplet states formation [1] and their lifetime is considerably longer than that of excited singlet ones, their influence on emission processes kinetics in the system cannot be neglected.

The stimulated emission process in OCE can be described by equation for photon flux density averaged over the resonator length [14]; the excited center distribution is also averaged over the film thickness. Such approach makes it impossible to determine the beam spatial structure and some other features, but gives enough information to determine possibility of population inversion, kinetic and energy parameters of the device being considered.

The second part of the model can be represented as a system of rate equations (5) with initial conditions (6):

$$\left\{\begin{array}{l} \dfrac{dN_g}{dt} = -k_A \cdot c^-(L) + \dfrac{N_T}{\tau_T} + \dfrac{N_g^*}{\tau_g^*}, \\ \dfrac{dN_T}{dt} = (1 - \varphi_S)k_A \cdot c^-(L) - \dfrac{N_T}{\tau_T} + k_{ST}N_S, \\ \dfrac{dN_S}{dt} = \varphi_S k_A \cdot c^-(L) - \left(\dfrac{1}{\tau_S} + k_{ST}\right)N_S - \sigma_S cI(N_S - N_g^*), \\ \dfrac{dN_g^*}{dt} = \sigma_S cI(N_S - N_g^*) + \dfrac{N_S}{\tau_S} - \dfrac{N_g^*}{\tau_g^*}, \\ \dfrac{dI}{dt} = \sigma_S cI(N_S - N_g^*) + \Omega\dfrac{N_S}{\tau_S} - \left(\beta + \dfrac{1}{2Lz}\ln\left(\dfrac{1}{r_1 \cdot r_2}\right)\right)cI, \end{array}\right. \qquad (5)$$

$$\left\{\begin{array}{l} N_T = N_S = N_g^* = 0 \\ N_g = N_0, \end{array}\right| t = 0, \qquad (6)$$

where N_S, N_T, N_g, N_g^* — singlet, triplet, ground and "excited ground" state populations, respectively; τ_S, τ_T, τ_g^*, singlet, triplet and "excited ground" state lifetime, respectively; N_0, luminophor molecular concentration in the film; I, photon flux density; σ_S, singlet state absorption cross-section; β, active loss coefficient in the medium; Lz, resonator optical length; r_1, r_2, mirror reflectances; c, light speed in the film; φ_S, singlet yield in the biradical recombination process; $c^-(L)$, AR concentration at anode surface; Ω, spontaneous emission portion falling into amplified modes.

The presented model was computed according to the developed algorithm using computer simulation and appropriate software for numerical solution of systems of nonlinear partial differential equations [1, 12, 13]. We should emphasize again that the distinguishing features of the model are: the account for the finiteness of DL charging rate, heterogeneous reaction on the electrodes surface rate, luminophor AR lifetime in solution volume; the emission processes computation in DPA film took into account the electron donor (AR) transport kinetics through cell volume. As a result of computation, we have obtained corresponding results describing kinetics of excited states and photon density flux (Figs. 1, 2).

Consideration of the results shows a fundamental possibility of threshold population of excited singlet levels and predominance of stimulated emission over spontaneous one (point 0, Fig. 1), which differs in principle from known results [1, 2].

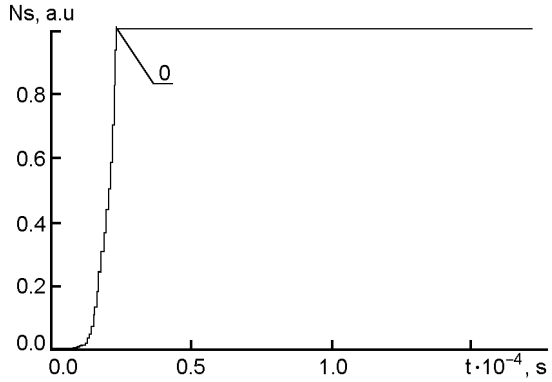

Fig. 1. Kinetics of excited singlet state population in OCE with modified electrode. Point 0 is the light generation threshold.

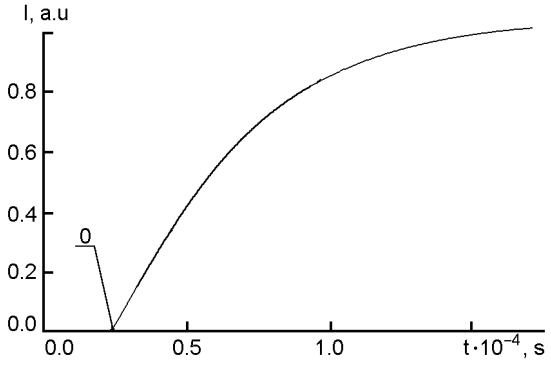

Fig. 2. Photon density flux kinetics in OCE with modified electrode. Point 0 is the light generation threshold.

Thus, our calculations show that in the proposed OCE model with working electrode modified by means of Langmuir-Blodgett and immobilized thin film of active substance — organic luminophor, — it is possible to achieve laser action with electrochemical pumping. It is obvious that a further theoretical investigation is urgent using physical and mathematical models taking into account all those complex processes occurring in OCE in stimulated emission mode, as well as development of real structures of such devices. Those certainly will find promising applications in various areas where coherent versatile, tunable, compact optical sources are necessary, such as sensors for biomedicine and ecology, signal and information converters for telecommunications, etc.

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Моделювання процесів в оптохемотронному випромінювачі з електродами, модифікованими за технологією Ленгмюра-Блоджетт

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За методом математичного моделювання вивчено можливість генерації світла в оптохемотронному пристрої рідиннофазної оптоелектроніки з робочим електродом, модифікованим за технологією Ленгмюра-Блоджетт нанесення тонких плівок. Розраховано кінетику випромінювальних центрів та густини потоку фотонів для подібної конфігурації когерентного оптохемотронного випромінювача з 9,10-дифенілантраценом у якості робочого електрохемілюмінофора, що знаходиться у плівці та в розчині. Показано можливість отримання інверсної населеності електронних рівнів молекул органічних люмінофорів та лазерної генерації при неоптичному електрохімічному збудженні в оптохемотронному випромінювачі.