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PHOTOSENSITIVE CHEMICALLY MODIFIED ELECTRODES FOR PHOTOGALVANIC CELLS

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Abstract

The problem of photosensitive chemically modified electrodes creation is under consideration in the present paper. Different methods of electrode surface chemical modification are applied to photogalvanic devices in order to transfer the photoelectrochemical processes in a solid phase. Photogalvanic cells based on thionine- ferrous, $[Ru(bipy)_3]^{2+}/[PtCl_6]^{2-}$, $[Ru(5\text{-}Clphen)_3]^{2+}/$ $[Fe(5\text{-}Clphen)_3]^{3+}$ systems are described with their components supported on solid polymeric matrix and in electropolymerized state.

The problem of creation of photosensitive molecular systems based on of photoinitiated electron transfer reactions is presented in series of papers [1-3]. The majority of photogalvanic devices proposed are homogeneous systems with sensitizer in the liquid phase. The only role of the electrode in this case is to pass the electrons into the electric chain. The disadvantages of such systems are the large outlay of the reagents, sufficiently large sizes and necessity of the hydrodynamical stimulation of the transport processes in liquid phase.

The next step is the development of the photogalvanic devices where components are attached to electrode giving chemically modified electrode. Such modification can be carried out through impregnation of sensitizer and/or quencher into the polymeric matrix attached to the electrode and direct polymerization of the sensitizer and/or quencher on the electrode. All this modification methods applied to well - known or slightly modified photogalvanic systems were used in presented work.

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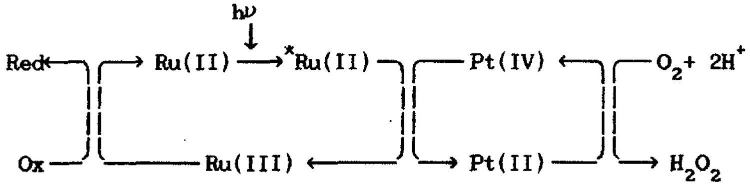
The simplest way in creation of solid- phase systems is to impregnate sensitizer into the polymeric electrolyte, ensuring the conductivity of the polymer layer. $Ru(bipy)_3^{2+}/[PtCl_6]^{2-}$ photogalvanic system [3] has been chosen for the realization of this modification method.

This system contains trisdipyridinum complex of ruthenium (II) as sensitizer and one of hexaacidic complexes of platinum (IV) as a quencher.

The scheme of the processes taking place in photogalvanic cell at light is following:



Thus, the formation of Ru(III) complex at light must be observed. This leads to the shift of inert electrode potential in positive direction. So, the complexes of Pt(IV) may be considered as peculiar catalyzers of summary process.

$$[Ru(bipy)_3]^{2+} + O_2 + 2H^+ \xrightleftharpoons{h\nu,\, PtCl_6^{2-}} [Ru(bipy)_3]^{3+} + H_2O_2$$

Reaction goes to the side of products only at light. When the light is switched off the reverse reaction takes place. It is the reaction between Ru(III) and hydrogen peroxide, making the system return to the initial state. Certainly, the cyclic change of photopotential at light and dark is observed. The value of photopotential change may reach 200 mV.

The discussed liquid- phase photogalvanic cell has some positive features, such as: reversibility of the passing processes, high values of the photogalvanic effect, high coefficient of charge separation.

It must be stressed that in this system unusual method of charge separation is applied. It deals with the fast reconstruction of ligand environment of Pt(III) complex, formed as a result of primary photochemical electron transfer. It is this fact which leads to the high value of charge separation coefficient.

But some disadvantages are characteristic for this system. They are: the necessity of lighted solution mixing, high outlay of reagents e.t.c. These disadvantages may be partly removed by organization of the photochemical processes in solid polymeric electrolyte i.e. by usage of chemically modified electrode.

It's known that $[Ru(bipy)_3]^{2+}$ saves its reversible electrochemical behavior in solid plymeric electrolyte MF-4SK [4].

On the basis of chemically modified electrode Pt/MF-4SK,$[Ru(bipy)_3]^{2+}$ the photogalvanic cell was made. The sensitizer was impregnated in solid plymeric electrolyte covered electrode by means of ion exchange (with concentration control) and the quencher stayed in solution.

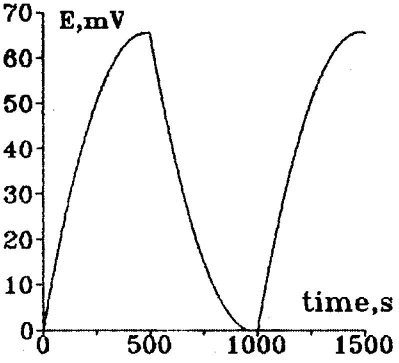


Fig.1 Photopotential dependence upon light irradiation.

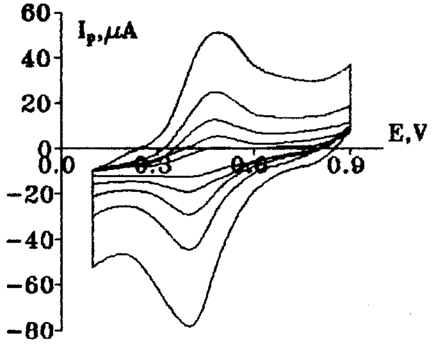


Fig.2 Cyclic voltammograms of thionine in MF-4SK.
Scan rates, V/s: 0.02, 0.05, 0.1, 0.2, 0.5.

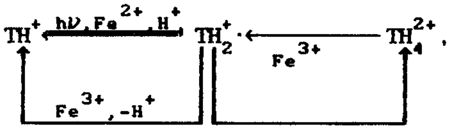
On Fig.1 the cyclic change of chemically modified electrode potential when the light is switched on and off is presented. This chart is analogous to one obtained in liquid- phase system. The differences are the following:

- slower kinetics of growth and drop of potential;
- maximum photogalvanic effect is 60-70 mV.

These peculiarities may be explained by decreasing of diffusion rates in membrane ($\sim 10^{-9} cm^2/s$) in comparison with solution ($\sim 10^{-6} cm^2/s$). Certainly, the formation of Ru(III) takes place in the whole volume of solid plymeric electrolyte, but its transport to the electrode surface is limited by the slow rates of charge diffusion. The dynamic equilibrium between formation and outlay of Ru(III) is influenced by the slow transport. This leads to smaller concentrations of Ru(III) at the electrode surface and decrease of photogalvanic effect in comparison with the liquid- phase cell.

The advantage of photogalvanic solid plymeric electrolyte cell is its relative compactness, little outlay of sensitizer (while its concentration near the electrode is very large), chemical stability and the absence of mixing. The main drawback is the presence of the liquid phase containing the quencher, leaving the dimensions of the cell sufficiently large.

The well - studied thionine - ferrous system has been chosen to study chemically modified electrodes with both sensitizer and quencher impregnated into the polymeric matrix of the solid polymeric electrolyte MF-4SK, analogous to Nafion. In this system thionine, the organic dye, serves as a sensitizer and iron(II) ions as a quencher. The short scheme of the reactions taking place in this system is following:



where TH^+- thionine, $TH_2^+\cdot$- semithionine, TH_4^{2+}- leucothionine.

At first we impregnated the mixture of sensitizer and quencher into membrane by means of ion exchange. Chemically modified electrode obtained was used as working in photogalvanic cell. We did not manage to record photogalvanic effect in described system. It's known, that the limiting stage of the processes in this system is the disproportioning of semithionine [5]:

$$2TH_2^{2+}\cdot + H^+ \longrightarrow TH^+ + TH_4^{2+},$$

Probability of this reaction decreases because of lower values of diffusion coefficient of semithionine in polymeric matrix in comparison with solution, and thus process follows the parallel path:

$$TH_2^+\cdot + Fe^{3+} \longrightarrow TH^+ + H^+ + Fe^{2+}$$

The resent works [6-9] devoted to thionine-ferrous system are dealt with the usage of chemically modified electrodes in the photogalvanic device. It was shown that thionine undergoes electrochemical polymerization on platinum, golden, glassy carbon and SnO_2- electrodes. The resulting chemically modified electrode may be used in photogalvanic cells, decreasing the dimensions of the device and the selectivity of the working electrode to the potential - determining redox pair. In order to obtain modified electrode with sensitizer and quencher situated in solid phase polymerization of thionine inside the membrane was carried out. Voltammograms of polythionine in the membrane are shown on Fig.2. The shape of the curves is analogous to one of polythionine on platinum electrode without membrane. After thionine polymerization in membrane the peaks potentials coincide with peak potentials of thionine polymerized on platinum electrode without membrane. This shows that polymerization in membrane is taken place and polymer obtained is similar to one obtained on clean platinum electrode. It is expected that mechanism of polymerization is the same both in solution [6] and in solid matrix, but decreasing of rate of polymerization due to common limitation of diffusion processes takes place.

Kinetics of polythionine film growth in membrane is slower then in solution [7] due to slowing down of diffusion transport of electroactive compound. Estimation of polythionine film thickness in solid polymeric electrolyte gives the value about 20 monolayers that is in good agreement with limit thicknesses of such films obtained on modified electrodes [8]. Values of peak currents after polymerization approximately coincides with ones before polymerization. This is dealing with the fact that from one hand the decreasing of diffusion coefficient up to $5\cdot10^{-13}cm^2/s$ [9] takes place and from the other hand the concentration of electroactive compound in film increases from value of 0.1 mol/dm^3 in membrane to 4.6 mol/dm^3 in the film. After the ion exchange impregnation of the quencher - Fe^{2+} ions into the membrane one can expect the obtaining of photogalvanic systems, analogous to known in solutions but in media of the solid polymeric electrolyte, where all reactions follows not in aqueous solution, but in "solution" in solid polymeric electrolyte.

In order to obtain the components in proper oxidation states electrode was treated with continuous (1hr., 0.0 V, SCE) cathodic polarization giving the iron ions in a reduced state and short (5 s, +0.5 V, SCE) anodic polarization giving the thionine film in oxidized state.

On Fig.4. the dependence of described electrode potential on time is presented. Potential drops after the switching on of the irradiation as a result of formation of reduced form of thionine - leucothionine in photoinduced electron - transfer reaction between excited thionine ions and ions of iron. While the light is switched off back reaction proceeds giving sensitizer and quencher in initial oxidation states. In comparison with analogous curve for the same system without solid polymeric

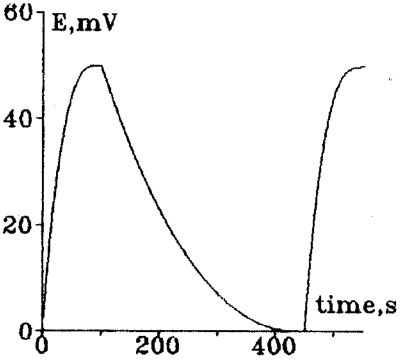


Fig.4 Photopotential dependence upon light irradiation. Polythionine modified electrode.

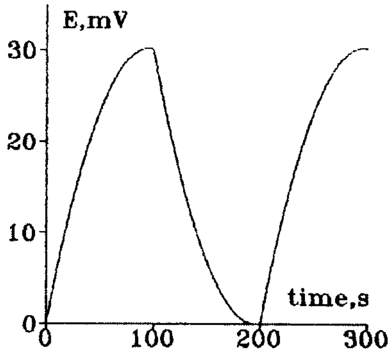
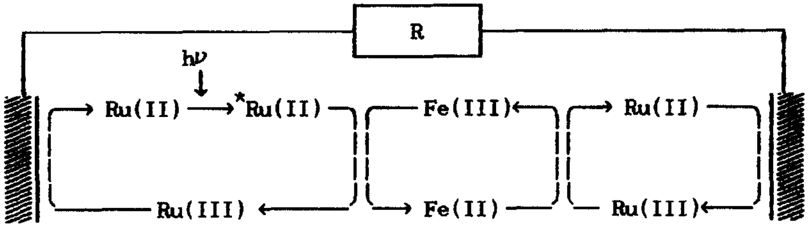


Fig.5 Photopotential dependence upon light irradiation. Polythionine in MF-4SK modified electrode.

electrolyte (Fig.5.) the decrease of photogalvanic effect and slower rates of photopotential growth are observed. These facts are explained mainly by slow Fe^{3+} transport rates in solid polymeric electrolyte. This drawback may be overcome by creation of chemically modified electrode with electronically conductive thin layers of senstizer and quencher both polymerized on the electrode.

We consider the 5-Clorophenathroline complexes of transition metals to be convenient objects for solution of this problem. Here we present the recent preliminary results of such studies.

It's known that *tris*-5-Clorophenanthroline complexes of Ru and Fe electropolymerize on the inert electrode surface giving transparent films with electronic redox conductivity [10]. At first we studied the photogalvanic effect in the single- layer system, where sensitizer (*poly*-$[Ru(5\text{-}Clphen)_3]$ was electropolymerized on the electrode and quencher ($[Fe(phen)_3]^{3+}$) stayed in solution. Under the light (452 nm.) irradiation the potential of the electrode increases due to the growth of the Ru^{III} concentration in the film (Fig.6). This increase of the concentration is connected with bimolecular photostimulated electron transfer reaction between $^{*}Ru^{II}$ and Fe^{III}.



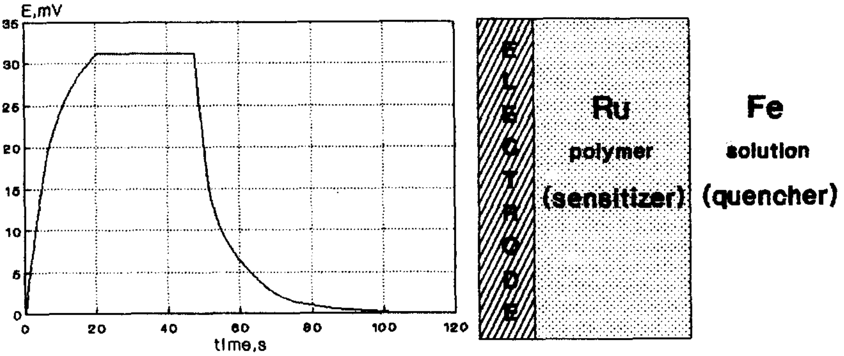


Fig.6 Dependence of Pt,*poly*-[Ru(5-Clphen)$_3$]|[Fe(phen)$_3$]$^{3+}$ system potential upon light irradiation.

Reaction is localized on the film surface and charge separation goes by diffusional way: liquid phase diffusion of iron(III) and electron hopping through the chains of the polymeric film.

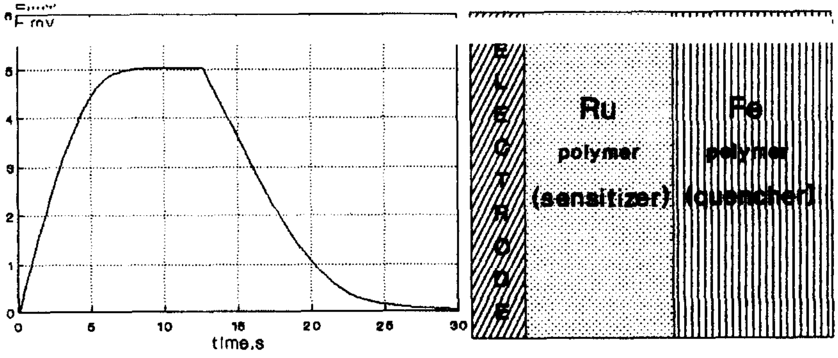


Fig.7 Dependence of Pt,*poly*-[Ru(5-Clphen)$_3$]|*poly*-[Fe(5-Clphen)$_3$] system potential upon light irradiation.

The next step in the development of this cell was creation of double-layer electrode with the layers of sensitizer and quencher polymerized consequently on the electrode surface. This is possible because sensitizer and quencher polymerization goes at the same potential (determined by ligand nature). Two cases are possible here: electrode|sensitizer|quencher and vice versa. First is represented on Fig.7.

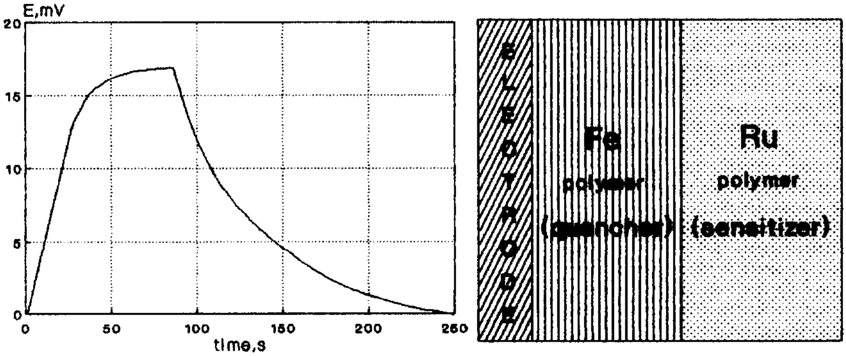


Fig.8 Dependence of Pt,*poly*-[Fe(5-Clphen)$_3$]|*poly*-[Ru(5-Clphen)$_3$] system potential upon light irradiation.

This scheme has a following drawback: because of the close position of quencher and sensitizer absorption bands the part of light is absorbed by the quencher layer. That's why the value of the photogalvanic effect is low. The change of layer order leads to the increase of the photogalvanic effect in the same conditions (Fig.8).

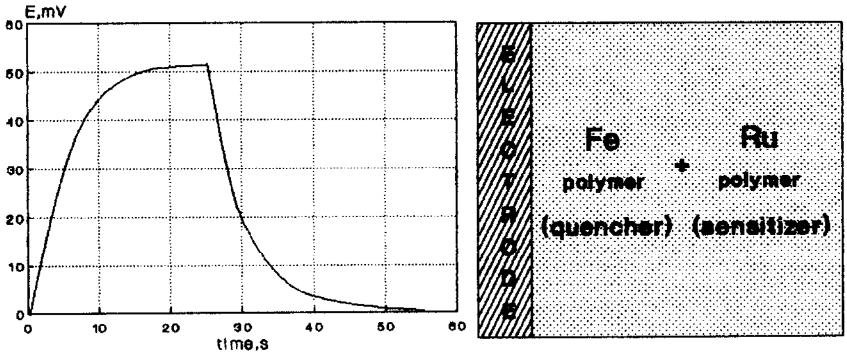


Fig.9 Dependence of Pt,*copoly*-[Fe(5-Clphen)$_3$],[Ru(5-Clphen)$_3$] system potential upon light irradiation.

The rate of the potential increase is determined by the rates of electron transfer in the nearest to electrode film layer. The charge diffusion coefficient in the Ru polymer is higher (we estimate it $\sim 10^{-11}$ cm^2/s) than that of Fe ($3 \cdot 10^{-12}$ cm^2/s). This causes the slow rate of the photopotential change in the case when ferrous polymer is on electrode.

The main drawback of the electrodes described above is that the photostimulated electron transfer reaction takes place on the interface of the film layers. In order to overcome this drawback the electrode with bulk reaction zone was proposed (Fig.9). Such electrode was prepared by electrocopolymerization of $[Fe(5\text{-}Clphen)_3]^{3+}$ and $[Ru(5\text{-}Clphen)_3]^{2+}$ from the equimolecular mixture of the complexes solution. This scheme allowed to obtain the photogalvanic effects higher than in all other cases.

Thus in this work we proposed different models of photosensitive chemically modified electrodes. We consider these electrodes to be perspective objects for creation of photochemical sensors and photogalvanic systems.

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