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Electromagnetic radiation during electrolysis of heavy water

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Abstract

The radiation in the visible and ultraviolet spectral regions during electrolysis of heavy water on nickel and palladium cathodes was determined for the first time. A sharp jump of the intensity photon flow was observed at a current density of higher than 125 mA/cm^2. A hypothesis about the relation of the electrochemiluminescence phenomenon during electrolysis of heavy water with the formation of fresh surfaces in consequence of the hydrogenous corrosion of the cathode material is formulated.

In connection with the discovery of so-called “cold fusion” we studied the model system used by Fleischmann and Pons [1], by the electrochemiluminescent (ECL) method. The experiments were performed on a specially constructed device, the scheme of which is shown in Fig. 1. It works in the photon counting mode and it is designed for registration of faint integral radiation in the range from units to 100000 counts per second. The basic block of the device (Fig. 2) was a metal box, with two compartments isolated from light. There was a photomultiplier with spectral response in the 160 to 600 nm region (the maximum of sensitivity corresponds to the 380–420 nm interval) in the first half. In the second compartment of the box, there was a quartz electrolytic cell (V = 80 cm^3) of inseparable type. As cathode we used a palladium sheet of 5.0 × 1.5 × 0.6 cm (geometrical area 15 cm^2, weight 9.16 g) and nickel foil of 4.0 × 2.5 × 0.2 cm (geometrical area 20 cm^2). The platinum spiral was used as anode. The concentration of the depolarizer ($LiClO_4$) in ordinary water (bidistillate) and in heavy water (99.9% D_2O) changes in the 0.1 to 2.0 mole/l range.

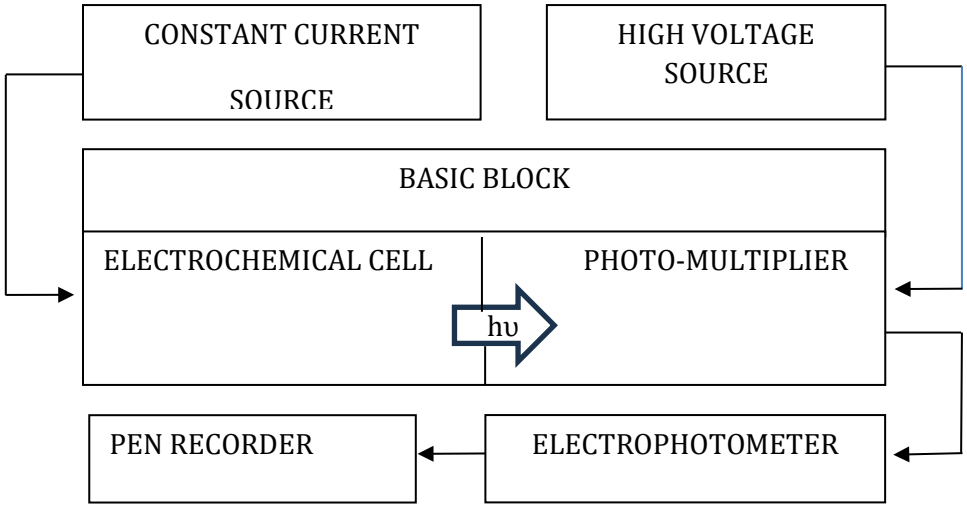

Figure 1. Schematic diagram of the device used in this electrochemiluminescent research.

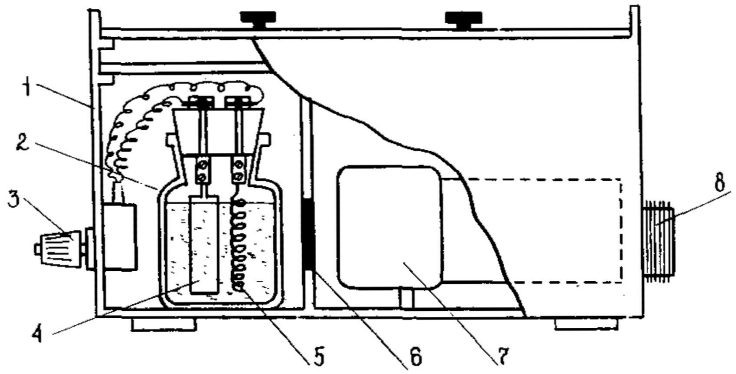

Figure 2. Structure of the basic block: (1) electrolytic cell, (2) case, (3) electric source connection, (4) Ni or Pd cathode, (5) platinum anode, (6) diaphragm, (7) connection with the registration device, (8) photomultiplier.

During the electrolysis of ordinary water, the intensity of light radiation corresponds to the background level (up to 50 counts/s). After the substitution of H_2O by heavy water, a considerable photon flow, of which the intensity depended on the current density and increases with time, was found (Fig. 3).

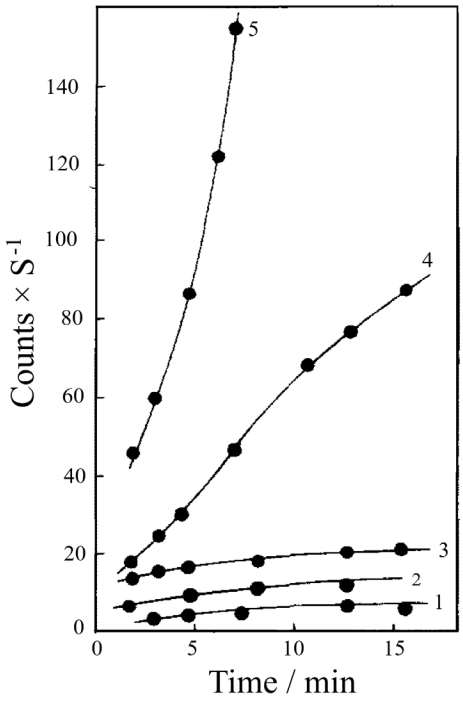

Figure 3. Change of the photon flow intensity with time at the current density (in mA/cm 2) 5 (1), 10 (2), 25 (3), 50 (4), 100 (5) (the material of the cathode is Ni).

In the current density range investigated, three regions can be distinguished. The intensity of radiation exceeded the background radiation marginally at i ≤ 25 mA/cm^2. The intensity radiation was several times larger than the background signal starting at i = 50 mA/cm^2 and more. The increase of the current over 125 mA/cm^2 leads to an uneven increase of the photon flow intensity to a value of 100000 counts/s and more (Fig. 4).

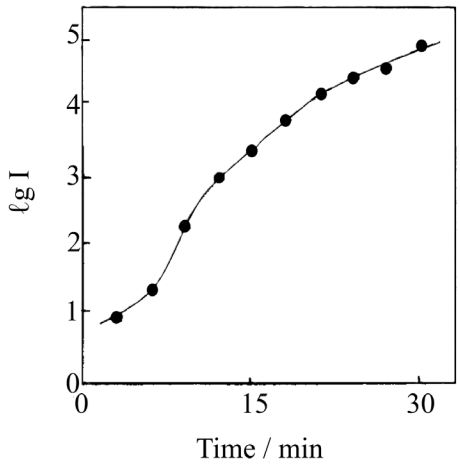

Figure 4. Dependence of the maximal photon flow intensity at the current density i = 125 mA/cm^2 in half-logarithmic coordinates.

The reproduction of this effect at a qualitative level was 100% (the number of the experiments was more than 150). However, even under identical conditions (current

density, concentration of the electrolyte, temperature and other) it is impossible to reproduce the value of the intensity radiation. For example, the intensity of the light flow for identical nickel electrodes, cut from one plate of foil, corresponds to values from 1000 to 100000 counts per second. This is why in Fig. 5 the determined maximal intensities of the radiation at different current densities are depicted.

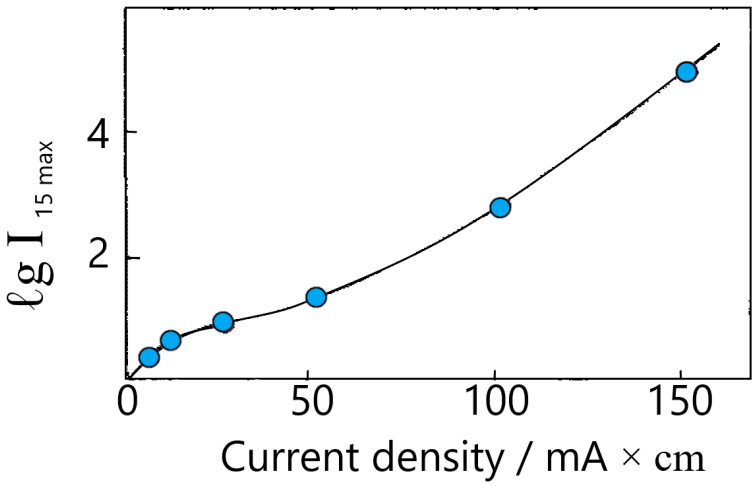

Figure 5. Dependence of the maximal photon flow intensity upon the current density 15 minutes after the electrolysis started, in half-logarithmic coordinates.

It was determined that the radiation intensity does not depend upon the concentration of the electrolyte in the lithium perchlorate concentration range 0.1 to 2.0 mole/ℓ.

At high current densities (i ≥ 125 mA/cm^2), strong heating of the solution and, in some cases, even evaporation to 40 cm^3 from the solution in 30–60 s takes place. This is why the investigations of the radiation intensity change during prolonged electrolysis were performed at i = 10 mA/cm^2 (Fig. 6). It was found that the radiation intensity reaches its maximum and then reduces to the background level respectively in 5–6 and 15–18 h after the start of electrolysis.

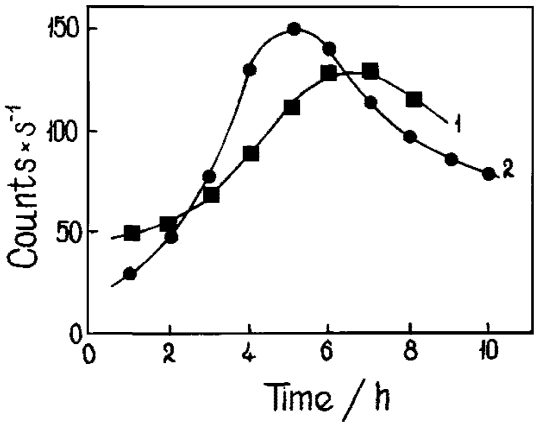

Figure 6. Change of the radiation intensity during the prolonged electrolysis of a 0.25M $LiClO_4$ solution on the Ni (1) and Pd (2) cathodes (i = l0 mA/cm^2).

In the stage of decreasing photon flow intensity in the experiment during prolonged electrolysis, we scoured surfaces of palladium electrode with an emery cloth. However, as is evident from Fig. 7, the renewal of the surfaces does not reproduce the characteristics of the cathode, as regards electromagnetic radiation. This experimental fact and also the fact of the low reproduction of the light signal for identical electrodes gives the basis for the assertion, that the main role in the ECL effect during electrolysis of heavy water is played by the structure of the crystalline lattice of the cathode material, which changes during the electrolysis.

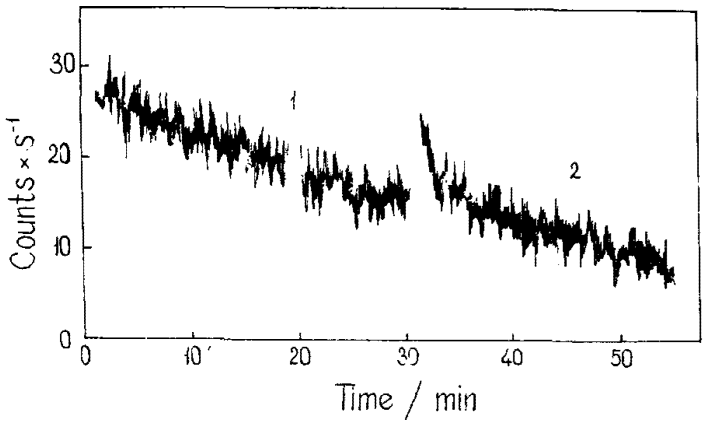

Figure 7. Radiation intensity before (1) and after (2) mechanical working up of the Pd electrode surface (i = 10 mA/cm^2).

In the saturation process of the cathode by deuterium, a complete alteration of the structure of the metal crystalline lattice occurs. After prolonged experiments at high current density the formation of a dark deposit on the electrode surfaces of both Ni and Pd was determined. The repeated use of such nickel electrodes gives negative results with respect to the ECL radiation.

The electrochemiluminescent properties of the more massive palladium electrode can be temporarily reproduced by thermal desorption of deuterium, which was accumulated on the electrode. Yet, later cracking and even disintegration of the palladium electrode takes place. After this, radiation during electrolysis of heavy water was not observed.

This suggests a hypothesis about the relation of the described experimental facts to the well-known phenomenon of triboemission of an electromagnetic wave under the destruction of ionic crystals and adhesive coating [2]. It is known that the triboluminescence phenomenon arises at the moment of formation of fresh surfaces, i.e. during the period of development of cracks. During the electrolytic saturation of transition metals by deuterium, hydrogen corrosion occurs, caused, in our opinion, by the origin of electromagnetic radiation. At the same time, the high concentration of lattice defects prevents the spreading of cracks, in consequence of which the radiation would not be observed at all. This well-known fact explains, in our opinion, the gradual decrease of the electrochemiluminescence intensity during prolonged electrolysis.

The triboemission phenomenon also explains the low reproduction of the radiation intensity value. It is obvious that the photon flow value will be conditioned by the initial density of defects in the specimen. However, as has been noted, the defect density can have a double effect. On the one hand, there must be a certain initial quantity of microcracks, at the development of which the electromagnetic radiation occurs. On the other hand, a larger number of crystalline structure defects leads to a weakening of the ECL properties.

As is known from experimental work with hydrides, the formation of microcracks is caused by an increase of the initial dimension of the metallic lattice at its saturation by hydrogen (or its isotopes), by the rise of the mechanical stresses and by the loss of the plasticity of the hydride phase. Nevertheless, the results of an X-ray structure analysis (diffractometer Cu-Kα radiation) for the cathodes used showed that the period of the crystalline lattice both of Pd and Ni during saturation by deuterium at atmospheric pressure practically did not change. The values of the lattice period of nonsaturated cathodes and cathodes, which lost their ECL properties, were respectively 0.35245 and 0.35265 nm for Ni and for Pd 0.38912 and 0.38938 nm, which is less than 0.1%. This gives the basis for the assumption that the fixed electromagnetic radiation is caused by the development of the initial density of defects in the specimen.

Yet, our hypothesis about the relation of the electromagnetic emission with the destruction of the crystalline lattice does not explain why the ECL phenomenon is not observed when ordinary water is used. Besides, even insignificant admixtures of H_2O in heavy water lead to a considerable fall of the radiation intensity. At 0.6 and 1.2 volumetric relative percent H_2O in D_2O, the radiation intensity decreased by 38% and 67% respectively (Fig. 8).

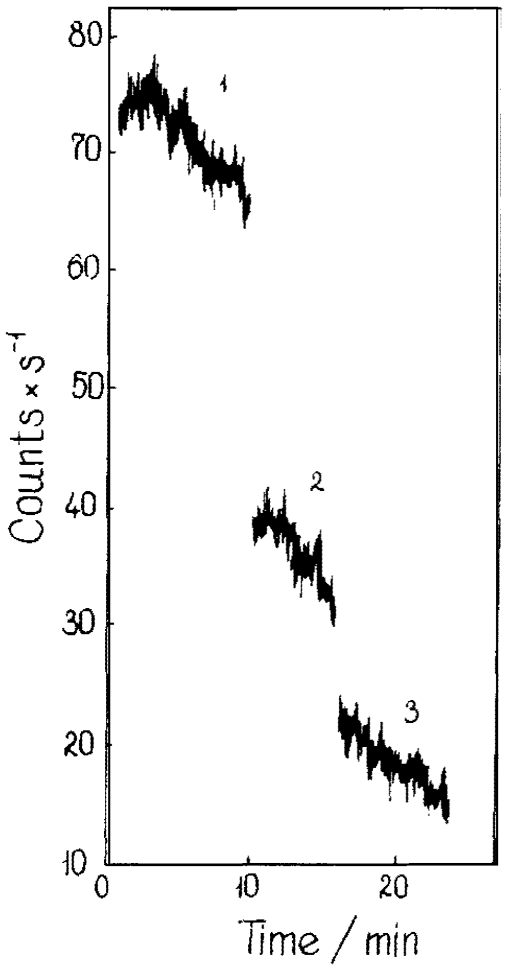

Figure 8. Influence of low quantities of H_2O on the radiation intensity: (1) initial signal, (2) and (3) signal after addition of 0.5 cm^3 and 1.0 cm^3 H_2O respectively (i = 10 mA/cm^2).

Thus, the presented experimental results support the fact that the process of electrolytic saturation by deuterium of transition metals, that are capable of absorption of considerable quantities of hydrogen or its isotopes (e.g. Ni and Pd), is accompanied by electromagnetic radiation of considerable intensity in the visible and ultraviolet spectral regions.

However, at present the phenomenon has been studied at a qualitative level only and further investigations are needed for the establishment of a quantitative dependence of the radiation intensity upon the different factors in the process of electrolysis.

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