Electrochemiluminescence in the reduction of uranyl ions on platinum in sulfuric acid solutions

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Electrochemiluminescence (ECL) accompanying the reduction of uranyl ions on a platinum cathode in sulfuric solutions in the presence of XeO_3 was observed and studied. At early stages of the electrolysis (at $0.34 < \varphi < 0.62$ V), the chemiluminescence reaction $U^V + XeO_3$ contributes mainly to the luminescence intensity, whereas at $\varphi < 0.32$ V, the contribution of the reaction $U^{IV} + XeO_3$ predominates. The transfer coefficient for the primary electrochemical stage, formation of U^V, was estimated: $\alpha = 0.46$—0.54. The high sensitivity of ECL to the state of the electrode surface is explained by the fact that the reduction of U^{VI} occurs on the most active sites only. The background chemiluminescence reactions, among which $U^V + O_2$ and $U^V + H_2O_2$ can be distinguished, were considered, and their contributions to ECL were determined.

Key words: electrochemiluminescence, electrochemical reduction, chemiluminescence, uranyl ions, xenon trioxide.

It is known[1,2] that the formation of uranium(V) in the reversible electrochemical reaction $UO_2^{2+} + e^- \rightleftharpoons UO_2^+$ is the primary act of reduction of UO_2^{2+} ions in low-acidic solutions. In high-acidic solutions, only a wave of irreversible two-electron reduction of U^{VI} is observed due to a high rate of disproportionation of U^V [1—4]:

$$UO_2^{2+} + 2\,e^- + 4\,H^+ \rightarrow U^{4+} + 2\,H_2O.$$

The reduction of uranyl ions on platinum electrodes occurs at potentials of hydrogen evolution, and the discharge of H^+ ions prevents observation of the corresponding wave on the voltammetric curves ($i = f(\varphi)$). The reaction of uranium(IV) with XeO_3 is accompanied by a bright chemiluminescence (CL),[5,6] whose intensity is independent of the presence of UO_2^{2+} ions, and an excess of XeO_3 proportional to the concentration of U^{IV} in the range from 10^{-10} to 10^{-4} mol L^{-1}. It was of interest to track the electrochemical reduction of uranyl through this reaction in the regions of current and potential values that are inaccessible for studying by other methods. In addition, as we have shown by our preliminary experiments, luminescence which is comparable in intensity is observed directly during the oxidation of uranium(V) by xenon trioxide. Thus, electrochemiluminescence (ECL) makes it possible to distinguish the reduction of UO_2^{2+} ions from the overall electrochemical process.

Experimental

The intensity of luminescence was measured on a setup consisting of an FEU-39A photoamplifier, a VS-22 high-voltage stabilized power source, and an EPPV-60M3 self-recording potentiometer. The spectral composition of luminescence was determined using boundary light filters. The electrochemical cell consists of two glass planar-bottom tubes with cone joints separated by an electrolytic swich with porous glass filters sealed-in on its ends. The working tube with a thermostatting water jacket arranged above a photocathode of the photoamplifier contained a smooth-platinum electrode (~0.5 cm^2) designed by Izgaryshev,[7] which served as a cathode. An anode (a platinum wire coil) was in another tube. An EVL-1M3 Ag/AgCl reference electrode was separated from the working electrode by an intermediate tube filled with an acid and by two electrolytic switches. The volume of solution in the cathodic space was ~30 mL. Measurements were carried out on a P-5827M potentiostat at 296 K with vigorous stirring using a mechanical stirrer. The potential sweep was 2 mV s^{-1}.

All solutions were prepared with bidistilled water. KCl (reagent grade) and hydrogen peroxide (analytical-purity grade) were used. Solutions of uranyl were obtained from UO_3 synthesized by the known procedure.[8] Solutions of XeO_3 were prepared from crystalline sodium perxenate Na_4XeO_6, which is rapidly hydrolyzed to XeO_3 in an acidic medium. Solutions of XeO_3 were standardized by titration with KI.[9] Concentrated sulfuric acid was purified by distillation, and its purity was monitored spectrophotometrically and fluorometrically. The concentration of H_2SO_4 in experiments was 1 mol L^{-1}. The concentration of XeO_3 was varied from $4 \cdot 10^{-5}$ to $2 \cdot 10^{-4}$ mol L^{-1}, and that of UO_2^{2+} was varied from $1 \cdot 10^{-4}$ to

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$9 \cdot 10^{-3}$ mol L^{-1}. The electrode potentials are presented relative to that of the standard hydrogen electrode.

Results and Discussion

Control measurements of the ECL intensity of pure solutions of H_2SO_4 and XeO_3 showed no luminescence. A weak ECL ($\sim 4 \cdot 10^5$ photon s^{-1} at the maximum) was observed in sulfuric acid solutions of uranyl (Fig. 1). The maximum in the ECL spectrum obtained by boundary light filters lies in the 500—520 nm region, which corresponds to the maximum in the photoluminescence spectrum of the UO_2^{2+} ion. This fact as well as the absence of other luminescent species in this system suggest that the uranyl ion is the emitter of ECL.

Electrochemiluminescence in O_2-containing acidic solutions of uranyl appears when the electrode potential decreases from the initial value of $\varphi_0 = 0.6$—0.8 V to $\varphi = 0.26$—0.25 V. A similar low-intensity luminescence has previously been observed in analogous experiments in 5 *M* H_2SO_4 at cathode potentials <0.3 V.[10] When φ further decreases, the ECL intensity (I_{ECL}) increases and passes through a maximum whose position varies in an interval from 0 to +0.14 V. At potentials $\varphi < -0.01$ V, the current through the cell increases sharply due to the discharge of H^+ ions, and at $\varphi = -0.1$ V it is already hundreds of milliamperes. This current increase is accompanied by a decrease in the luminescence intensity. After the cell was switched-off from the potentiostat, we observed different dynamics of the luminescence decay. For example, when the maximum of

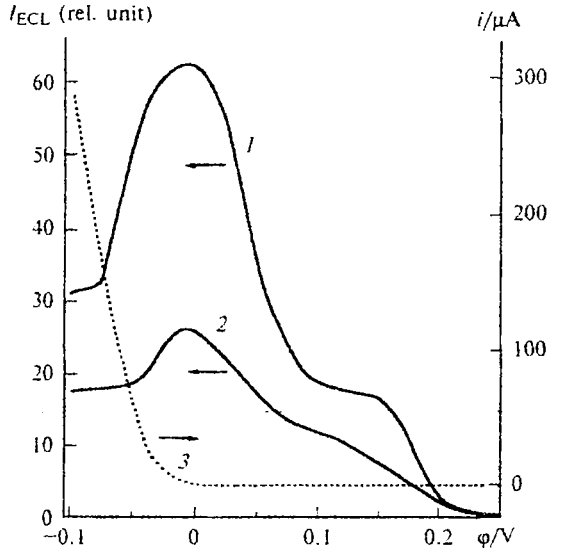

Fig. 1. Dependences of the ECL intensity (I_{ECL}/rel. units, curves *1*, *2*) and current *i* through the cell on the electrode potential φ in the UO_2^{2+}—O_2 system: *1*, first cycle of electrode polarization; *2*, repeated cycle; and *3*, voltammetric dependence for both cycles. $[UO_2^{2+}]_0 = 9 \cdot 10^{-3}$ mol L^{-1}, $[H_2SO_4] = 1$ mol L^{-1}.

I_{ECL} was observed at $\varphi \approx 0$ V, the luminescence decreased sharply by 5—6 times (and the electrode potential increased rapidly almost to the initial value), and then its intensity (*I*) decreased rather slowly. When two successive cycles of cathodic reduction were performed by the same scheme, the ECL intensity decreased substantially in the second cycle (see Fig. 1, curve *2*). Removal of oxygen from the system by bubbling of an inert gas resulted in the disappearance of the luminescence (this fact has been observed earlier[10]).

It is reasonable to attribute the observed ECL to the appearance of low-valence forms of uranium, U^{IV} and UO_2^+, which are oxidized by dissolved oxygen and hydrogen peroxide formed during electrochemical reduction of O_2.[11] Special experiments on oxidation of uranium(IV) by dioxygen demonstrated that the luminescence is absent under our conditions. The fraction of H_2O_2 formed on the platinum electrode is low, ≤6% of the amount of reduced O_2.[11] Model experiments with solutions of H_2O_2 and U^{IV} showed that the luminescence intensity in this reaction is low, and its contribution to the overall ECL intensity (even under the assumption of 100% yield with respect to the current during the reduction of UO_2^{2+} ions) does not exceed 5—10%. Thus, the ECL observed is mainly related to the oxidation of uranium(V) by dioxygen and hydrogen peroxide followed by the formation of UO_2^{2+} in the electron-excited state ($^*UO_2^{2+}$). This is confirmed by our previous observation of CL in independent experiments on the interaction of O_2 with UO_2^+ ions generated by the chemical reduction of uranyl ions by europium(II). The oxidation of U^V has a complex free radical character; the reaction

$$UO_2^+ + OH^\cdot + H^+ \rightarrow {}^*UO_2^{2+} + H_2O$$

is most likely the direct light-emitting stage, because the amount of energy necessary for the excitation of the uranyl ion is evolved in this reaction.

Thus, it can be expected that the ECL intensity, which is proportional to the concentration of U^V at a sufficient concentration of oxygen in the solution, reproduces the wave of one-electron reduction of UO_2^{2+} ions. It has been shown in a special study[3] of the reduction of uranyl on a platinum cathode in 1 *M* H_2SO_4 that this wave corresponding to the overall two-electron process

$$UO_2^{2+} + 4\,H^+ + 2\,e^- \rightarrow U^{4+} + 2\,H_2O$$

(due to a high rate of disproportionation of U^V in sulfuric acid solutions[12]: $k_{U^V+U^V} = 5.4 \cdot 10^4$ L mol^{-1} s^{-1}) is completely disguised (under standard conditions) on voltammetric curves by the discharge of H^+ ions. ECL measurements make it possible to observe the primary stage (one-electron reduction of uranyl) and detect the initial region of the corresponding wave already at high positive potentials. However, further, at potentials of hydrogen evolution when the current of uranyl reduction (and, correspondingly, the rate of generation of U^V)

should reach the diffusion limit, a decrease in I_{ECL} is observed. This phenomenon can be due to several reasons. First, the near-electrode layer is depleted of dissolved oxygen because of its replacement by hydrogen and reduction by H$^{\cdot}$ atoms that formed, and due to the high rates of the reactions

$$OH^{\cdot} + H_2 \rightarrow H^{\cdot} + H_2O \quad \text{and} \quad OH^{\cdot} + H^{\cdot} \rightarrow H_2O$$

the concentration of the direct participants of the chemiluminescence stage, OH$^{\cdot}$ radicals, also decreases. In addition, the H$^{\cdot}$ atoms efficiently oxidize U^{V} to U^{VI} [13] ($k_{U^{V}+H^{\cdot}} > 10^7$ L mol^{-1} s^{-1}), which explains the previously observed[2] decrease in the yield of U^{V} at potentials of hydrogen evolution.

The sharp decrease in I_{ECL} observed after the current was switched-off indicates the same sharp decrease in the concentration of U^{V} in the near-electrode space. The remaining luminescence is most likely due to the oxidation of a minor amount of U^{V} in the bulk solution and the oxidation of U^{IV} by hydrogen peroxide formed.

As suggested in Ref. 3, hydrogen adsorbed on platinum plays an important role in the electrochemical reduction of uranyl, because the wave of reduction of UO_2^{2+} is shifted by 0.1—0.2 V toward positive potentials after the special pretreatment of the electrode: many cycles in the +0.475 to −0.05 V range or sufficiently prolonged exposure to a low potential ($\varphi < -1.0$ V). It is most likely that it was the formation of precisely this "active" hydrogen that was observed in experiments in which a shift of the maximum of I_{ECL} by 0.10—0.14 V toward positive potentials was observed (Fig. 2, *a*) after a preliminary sufficiently prolonged (15—20 h) exposure of the electrode to the hydrogen-saturated acid, and a slow (over several minutes) luminescence decay and an increase in the electrode potential (see Fig. 2, *b*) was observed after the cessation of electrolysis. In this case, the wave of U^{VI} reduction observed as ECL is much more pronounced. It is most likely that an addition process resulting in the generation of UO_2^{+} ions occurs along with the electrochemical process. The reduction of uranyl ions by dissolved molecular hydrogen catalyzed with the platinum surface could be this additional process.[4]

The appearance of "active" hydrogen is a consequence of a special state of the platinum surface. It has been proved[14] that the above-described treatment of the electrode increases the coverage of the surface by very active, although scanty metal atoms, which play a major role in electrochemical processes. The predominant electrochemical reduction of UO_2^{2+} or its chemical reduction by dissolved H_2 should occur on precisely those low-coordinated Pt atoms[14] (active sites), and their blocking, correspondingly, results in a sharp retardation of this process.

The decisive role of the state of the platinum surface is also indicated by our experiments with an electrode subjected to preliminary anodic polarization for 0.5 h at potentials of oxygen evolution and a high current density. After this treatment, the initial electrode potential in the solution under study increased to $\varphi_0 = +1.45$ V (before the treatment it usually ranged from +0.6 to +0.8 V in solutions of uranyl), which indicates the formation of a compact film of platinum oxides on the surface.[15] This

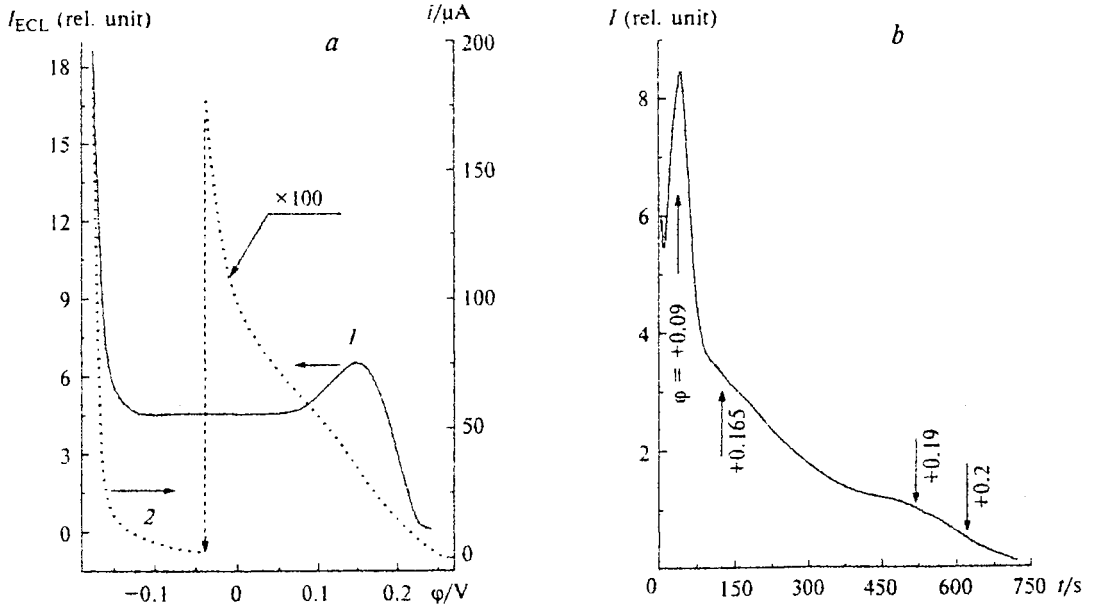

Fig. 2. *a*. Dependences of the ECL intensity (I_{ECL}/rel. units, curve *1*) and current *i* (curve *2*) through the cell on the electrode potential φ in the UO_2^{2+}—O_2 system after preliminary exposure of the electrode to an acid solution saturated with hydrogen. *b*. Decrease in the luminescence intensity (*I*/rel. units) after switching-off the cell. The marks of potential are shown by arrows. $[UO_2^{2+}]_0 = 9 \cdot 10^{-3}$ mol L^{-1}, $[H_2SO_4] = 1$ mol L^{-1}.

electrode exhibits no ECL even at negative potentials and a current through the cell of ~0.5 A. A weak luminescence appears only after the cycle of cathodic polarization (the partial reduction of the platinum surface), and in the next cycle its intensity reaches the standard value. In these experiments, the absence of ECL is direct evidence of a complete blocking of the electroreduction of uranyl ions on the surface covered with the oxide film, despite the negative polarization of the electrode and vigorous hydrogen evolution. As is known, the most active sites on the platinum surface adsorb substances from the solution more rapidly than other sites and form with them the strongest bonds. Oxides formed by them should have a higher stability and be reduced last. It is known[14] that hydrated oxide films formed on platinum during anodic polarization of the electrode contain components that are slowly reduced even at $\varphi < 0$ V, and no ECL is observed until their reduction occurs. Unlike uranyl ions, the discharge of H^+ ions occurs also on the partially oxidized surface at less active sites (most likely due to a sufficiently high energy of the Pt—H bond and the spillover effect — a transfer of H˙ atoms from more active to less active sites).

In the system described, the reaction of U^V with H_2O_2 formed on the cathode can make a certain contribution to ECL. To check this assumption, we polarized the electrode in a solution of uranyl ($[UO_2^{2+}]_0 = 5 \cdot 10^{-3}$ mol L^{-1}) to $\varphi = -0.1$ V and then added hydrogen peroxide ($[H_2O_2]_0 = 5 \cdot 10^{-2}$ mol L^{-1}), which was accompanied by a jumpwise increase in I_{ECL} by two orders of magnitude. The luminescence observed is the result of chemiluminescence oxidation of U^{IV} and U^V by hydrogen peroxide. After switching-off the cell, the luminescence intensity immediately decreases by 4.7 times and then decreases exponentially (Fig. 3). The fast decrease in luminescence is most likely due to the reactions of U^V, and the slow decrease is the result of the reactions of U^{IV}. In fact, the bimolecular rate

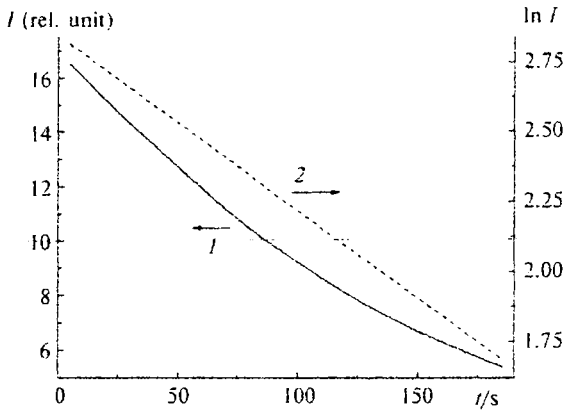

Fig. 3. Time dependence of the luminescence intensity (I/rel. units, curve *1*) and its linear anamorphosis (curve *2*) after the end of electrolysis in the UO_2^{2+}—H_2O_2 system. $[UO_2^{2+}]_0 = 5 \cdot 10^{-3}$ mol L^{-1}, $[H_2O_2]_0 = 5 \cdot 10^{-2}$ mol L^{-1}, $[H_2SO_4] = 1$ mol L^{-1}.

constant obtained from the curve of decreasing I is 0.126 L mol^{-1} s^{-1}, which corresponds to the reaction $U^{IV} + H_2O_2$ (the authors of Ref. 16 present $k_{U^{IV}+H_2O_2} = 0.41$ L mol^{-1} s^{-1} for 0.4 *M* H_2SO_4, and it should be taken into account that the reaction is substantially retarded with increasing acid concentration). The ratio of intensities of the fast to slow components of I indicates that the CL intensity in the reaction $U^V + H_2O_2$ is much higher than that in the reaction $U^{IV} + H_2O_2$, due, first of all, to its high rate[13]: $k_{U^V+H_2O_2} = 55$ L mol^{-1} s^{-1}. In addition, U^{IV} is accumulated in solution, and its concentration to the end of electrolysis should be much higher than that of U^V. However, if electrolysis is performed from the very beginning in the presence of the same amount of H_2O_2, the luminescence intensity immediately decreases almost to zero after cessation of electrolysis. This implies that at a sufficiently high concentration of hydrogen peroxide the reaction $U^V + H_2O_2$ competes successfully with the reaction $U^V + U^V$, and the amount of U^{IV} formed is low.

The experiments performed make it possible to estimate the contribution of the reaction $U^V + H_2O_2$ to ECL of the U^{VI}—O_2 system. Taking into account that the solubility of O_2 in 1 *M* H_2SO_4 is 1.35 times[17] lower than that in water and the yield of H_2O_2 on the platinum cathode is <6%,[11] we found that the contribution of the considered reaction to the overall ECL intensity does not exceed 3%. Thus, ECL observed with the electroreduction of uranyl ions in the presence of dissolved O_2 is mainly due to the reaction of the latter with U^V formed in the primary electrochemical stage.

The reduction of UO_2^{2+} in the presence of XeO_3 exhibits a brighter ECL (Fig. 4, *a*), whose intensity exceeds, in some cases, that of ECL of pure uranyl solutions by 2—3 orders of magnitude; however, the magnitude of the effect is poorly reproducible. The ECL spectrum corresponds to that of photoluminescence of uranyl ions, which, as in the cases considered above, proves chemiexcitation of UO_2^{2+} ions during the process. After interruption of electrolysis, the luminescence decays slowly (see Fig. 4, *b*), indicating that chemiluminescence reactions proceed in the bulk solution. An increase in the concentration of UO_2^{2+} leads to an increase in the luminescence intensity both during electrolysis and after its cessation. It is difficult to reproduce intense ECL (with a maximum intensity of ~$3 \cdot 10^8$ photon s^{-1}) in this system, which is most likely related to both a high sensitivity of the reduction of uranyl to the state of the platinum surface and specific features of the chemical behavior of dilute solutions of XeO_3. Note in this connection that a strong dependence of the electrocatalytic properties of platinum electrodes on their pre-history and methods of treatment is commonly known, as well as the difficulties associated with the preparation of a specific, "standard" state of the platinum surface. It is clear that in experiments when intense ECL is observed, we deal with a highly active state of

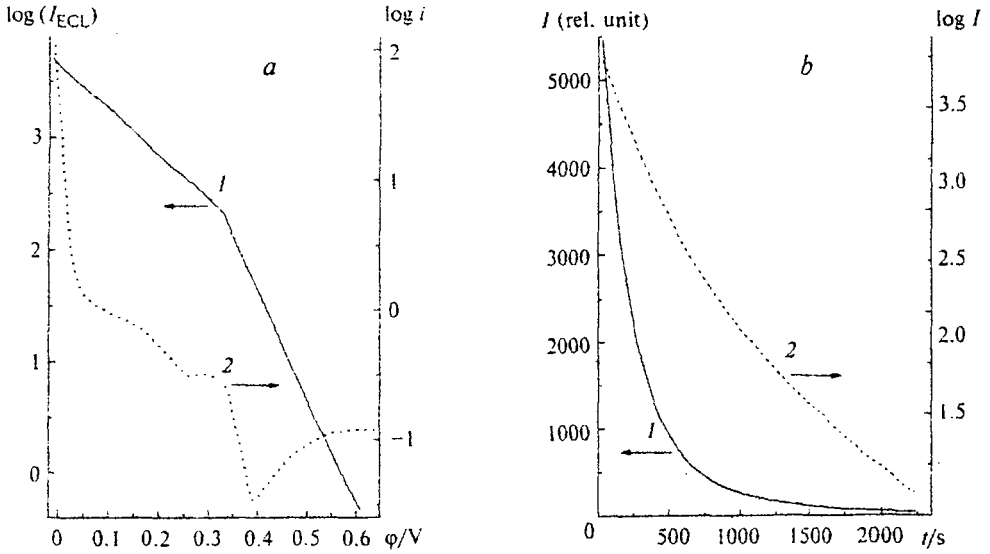

Fig. 4. *a*, Dependences of the ECL intensity (I_{ECL}/rel. units, curve *1*) and current (i/μA, curve *2*) on the electrode potential φ in the UO_2^{2+}–XeO_3 system. *b*, Dependence of the luminescence intensity (I/rel. units, curve *1*) and log$I$ (curve *2*) on time after the end of electrolysis. $[UO_2^{2+}]_0 = 9 \cdot 10^{-3}$ mol L^{-1}, $[XeO_3]_0 = 1.84 \cdot 10^{-4}$ mol L^{-1}, $[H_2SO_4] = 1$ mol L^{-1}.

the electrode surface and, correspondingly, a high rate of electroreduction of uranyl ions on this surface. In these cases, the beginning of the appearance of luminescence is recorded already at $\varphi \approx +0.62$—0.6 V, and with further potential decrease, it rapidly increases in parallel with an increase in the current through the cell. The highest luminescence intensity is achieved at maximum currents and potentials of H_2 evolution.

The following photoreactions occur in the cathodic space in the presence of XeO_3. First, U^{IV} formed on the cathode is oxidized by xenon trioxide, which is accompanied by very intense CL.[5,6] It is assumed that the oxidation of U^V formed as an intermediate product is the photostage. Second, as we have shown by the previous independent experiments, luminescence comparable in intensity is also observed directly with the oxidation of uranium(V). Thus, ECL observed in this system reflects the overall process of electroreduction of uranyl ions with the formation of uranium(IV, V). At a considerable excess of XeO_3, the luminescence intensity is proportional to the concentration of the reagents[5,6]:

$$I = \eta_{CL} \cdot k_{U^{IV,V}+Xe^{VI}} \cdot [U^{IV,V}] \cdot [XeO_3] = \text{const} \cdot [U^{IV,V}],$$

where η_{CL} is the quantum yield of CL of the corresponding reaction, equal to the ratio of the number of luminescent photons to that of the emitter molecules formed; $k_{U^{IV,V}+Xe^{VI}}$ is the rate constant of this reaction; and $[U^{IV,V}]$ is the concentration of U^{IV} or U^V, respectively.

In the presence of uranyl ions, a low-intensity luminescence can also appear when H_2O_2 reacts with XeO_3,[18] distorting the true picture of the process. However, since the rate of formation of hydrogen peroxide from O_2 slightly changes in the potential range from +0.7 to +0.4 V [11] and no luminescence is observed at $\varphi >$ +0.63 V, we may suggest that the contribution of the considered reaction to the overall ECL intensity is negligible.

Thus, the high intensity of CL of the reactions involving XeO_3 makes it possible to detect the very beginning of the electrochemical reduction of U^{VI} at relatively high positive potentials (~0.6 V). Since no adsorbed hydrogen is present on the platinum surface under these conditions, the question arises about the mechanism of so early an appearance of low-valence forms of uranium and the effect of xenon trioxide on it.

In this connection, it is of interest to compare the luminescence observed with the previously studied ECL of solutions of UO_2^{2+} (in 5 *M* H_2SO_4) in the presence of another strong oxidant, ozone.[6,10] In this case, the reaction $U^{IV} + O_3$ is chemiluminescent. The existence of CL in the oxidation of U^V can be assumed with a high probability.[6] The appearance of a weak luminescence (in the form of a "step") was observed at $\varphi = +0.8$ V, and then, after decreasing the potential to ~+0.3 V, I_{ECL} begins to increase rapidly. ECL appearing at $\varphi < 0.35$ V was ascribed to the appearance of U^{IV} on the cathode followed by its subsequent oxidation with ozone. The weak ECL at higher potentials can be due to uranyl-sensitized electrochemically initiated decomposition of ozone sorbed on the electrode surface: at $\varphi < +0.85$ V the platinum surface is mainly liberated from chemisorbed oxygen[19] and becomes accessible for other species in the solution. Thus, the appearance of intense ECL in the presence of O_3 correlates satisfactorily with the appearance of luminescence in the system with O_2.

Based on these data, we may assume that XeO_3 exerts a specific effect on the state of the platinum

electrode, which facilitates substantially the reduction of UO_2^{2+}. If we hold a very plausible, in our opinion, idea about the leading role of a small number of active sites in electrocatalytic processes,[14] the appearance of low-valence forms of uranium at high positive potentials should be considered as a result of action of the most active sites, which are inevitably poisoned, under standard conditions, by microadmixtures present in the solutions and therefore cannot manifest themselves. It can be assumed that XeO_3 provides efficient purification of the platinum surface and deblocking of these sites.

Data on the electrochemical behavior of xenon trioxide are scarce. As has been reported previously,[20] XeO_3 interacts with the platinum electrode surface, oxidizing it, and the voltammetric characteristics obtained in this case are similar to the curve for solutions of O_2, *i.e.*, correspond to the reduction of chemisorbed oxygen. As demonstrated in experiments with a vitreous carbon electrode that is inert under these conditions, xenon trioxide itself is electrochemically reduced only at low negative potentials ($E_{1/2} < -0.7$ V). The oxidation state of a platinum surface can be estimated from the initial potential of the electrode φ_0 in a solution of XeO_3. In cases where an intense luminescence was observed, the high value $\varphi_0 = +0.9$ to $+1.0$ V was established. At these potentials, the platinum surface is covered with a monolayer of OH groups, and this process is reversible[19]: after the electrode was placed into a pure acid, we observed a decrease in its potential for 2—3 min. As is well known, oxygen-containing species are strongly sorbed on the platinum surface and displace other molecules from it. This is the basis for the procedure of purification of electrodes by their cyclic polarization. During cathodic polarization of this electrode, the OH monolayer is reduced, and the pure platinum surface with highly active sites becomes accessible. It is likely that admixtures that suppress the electrocatalytic activity of these sites should be sorbed immediately on them. If this does not take place (as we can see from the presence of ECL), the process of continuous renewal of the platinum surface should occur. This renewal can occur due to the continuous (at $\varphi < +0.8$ V) "chemical oxidation—electrochemical reduction" cycle with continuous regeneration of active sites. In addition, under these conditions, organic contaminations and CO should efficiently be removed from the platinum surface due to their oxidation to CO_2.

After the preliminary anodic treatment of the electrode, no ECL is observed in the UO_2^{2+}—XeO_3 and UO_2^{2+}—O_2 systems, and it appears only after several cycles of cathodic polarization of this electrode. The absence of luminescence indicating the absence of low-valence forms of uranium in the solution is probably due to the same reason: blocking of the most active sites on the platinum surface by a layer of the stable oxide phase. The differences in potentials at which intense ECL appears in the systems with XeO_3 and O_3 can be related to the formation of various types of chemisorbed oxygen on the electrode surface. Unlike XeO_3, ozone is a more rigid oxidant, and the high initial potential $\varphi_0 = 1.6$ V is immediately established in its solution.[10] At this potential, the platinum surface is completely covered with strongly chemisorbed oxygen (in the form of PtO),[14,19] whose reduction is hindered. Another form of chemisorbed oxygen, surface PtOH groups, are formed in solutions of XeO_3. As has previously been shown,[14] the OH groups present on the platinum electrode surface possess a very high electrocatalytic activity and can exist in a wide potential range ($\varphi \approx 0.2$—0.8 V). It cannot be ruled out that these species facilitate the electron transfer by the formation of a sufficiently strong coordination bond with uranyl ions, which results in the reduction of UO_2^{2+} at relatively high potentials.

After switching-off the current (see Fig. 4, *b*) the luminescence intensity decreases slowly. Since the rate of disproportionation of U^V and its oxidation by xenon trioxide are sufficiently high (the characteristic time of the latter is $\sim 10^2$ s at the used concentration of XeO_3),[24] the luminescence observed in this case should be attributed to the chemiluminescence reaction of a more stable product, namely uranium(IV), with XeO_3. Although the curve of the decreasing CL intensity is not linearized in the semilogarithmic coordinates, which does not allow one to obtain an exact value of the rate constant of the process, the time of its occurrence agrees well with the known data for the reaction $U^{4+} + XeO_3$.[6,22] Thus, this is precisely the reaction that makes the main contribution to the CL intensity after cessation of electrolysis.

We have previously[21] determined the rate constant of the reaction of U^V with XeO_3 in 0.1 *M* $HClO_4$ (depending on the concentration of uranyl ions with which it forms a complex, the rate constant varies from $2.9 \cdot 10^2$ to $6.5 \cdot 10^2$ L mol s^{-1}). Assuming that the rate of this reaction does not depend strongly on the acidity, the value presented above can be used for estimation of the ratio of the rates of the fastest reactions of U^V:

$$U^V + U^V \ (v_1) \quad \text{and} \quad U^V + XeO_3 \ (v_2).$$

Since

$$v_1/v_2 = k_{U^V+U^V} \cdot [U^V]^2/(k_{U^V+Xe^{VI}} \cdot [U^V] \cdot [XeO_3]) > \\ > 2 \cdot 10^2 \cdot [U^V] \cdot [XeO_3]^{-1},$$

a substantial contribution of the oxidation of uranium(V) to the overall ECL intensity can be expected in our experiments only at $[U^V] < 10^{-6}$ mol L^{-1}, *i.e.*, at early stages of electrolysis (at higher potentials). In this case, we can write for the chemiluminescence reaction[6] $I_{ECL} = \eta_{CL} \cdot v_2 = \eta_{CL} \cdot dU^V/dt$ and for the electrochemical reaction $dU^V/dt = \eta_{EC} \cdot i_U$ (where i_U is the current consumed in the reduction of uranyl ions, and η_{EC} is the yield of U^V with respect to current). Assuming that the primary electrochemical stage of charge transfer with the formation of uranium(V) is the limiting stage of the process and, hence, the rate of its consumption is equal to the rate of formation, we obtain $I_{ECL} = \eta_{CL} \cdot \eta_{EC} \cdot i_U$,

or $\log(I_{ECL}) = \log(i_U) + \text{const}$. As can be seen in Fig. 4, *a*, which presents two almost linear regions on the plot $\log(I_{ECL}) = f(\varphi)$, it should be admitted that the $\log(i_U)$ value also changes linearly when the potential ($\Delta\varphi$) is varied, *i.e.*, $\log(i_U) = \text{const} + b \cdot \Delta\varphi$. This is just a variety of the Tafel dependence for the reduction of U^{VI}. Then $b = 2.303RT(\alpha \cdot n \cdot F)^{-1} = 0.058(\alpha \cdot n)^{-1}$, where α is the transfer coefficient, and n is the number of transferred electrons.[23] In the case considered, $n = 1$, and from the slope of the region at $\varphi > 0.34$ V we obtain $b = 0.107$, from where $\alpha = 0.54$ (which is close to the theoretical value $\alpha = 0.5$ for the simple electron transfer). Another linear region (at $\varphi < 0.32$ V) corresponds, evidently, to CL of the reaction $U^{IV} + XeO_3$, which here becomes predominant. For this region, $b = 0.252$, and taking into account the overall two-electron reduction of uranyl ions ($n = 2$), for the primary electrochemical stage we obtain $\alpha = 0.46$, which is close to the previously obtained value.

Thus, observed ECL allows one, due to its selectivity, to distinguish the component directly related to the reduction of uranyl ions from the complex electrochemical reduction of a solution and to obtain an estimate of the purely electrochemical magnitude α for its primary stage — formation of U^V.

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