Russian Chemical Reviews **76** (3) 235 – 251 (2007) © 2007 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2007v076n03ABEH003638

Physicochemical properties of plasma – solution systems and prospects for their use in technology

A G Zakharov, A I Maksimov, Yu V Titova

Contents

I.	Introduction	235
II.	Plasma – solution systems	235
III.	The effect of gas discharges on physicochemical properties of solutions	237
IV.	Plasma-initiated chemical processes in solution	238
V.	Potentials and prospects of plasma initiation of industrial processes in aqueous solutions	246
VI.	Conclusion	250

Abstract. Gas discharge initiation of chemical processes in electrolyte solutions is considered. Data on the types of chemical transformations in plasma – solution systems are presented. The processes of generation of primary reactive species in solutions under gas discharge and the key routes for their further reactions are analysed. The prospects for practical application of plasma – solution systems in solving technological and environmental problems are considered. The bibliography includes 109 references.

I. Introduction

Nonequilibrium gas-discharge plasma finds practical application in implementation of numerous physicochemical processes [1] due to its extremely high chemical activity at relatively low temperatures of treated materials. As a penalty, the high reactivity entails low selectivity of chemical reactions initiated by plasma. This necessitates a search for such conditions that would combine the high reactivity of plasma with the selectivity of its effect. The fundamental way for solving this problem is presented by the plasma activation of chemical reactions in electrolyte solutions. Successful realisation of these processes requires the knowledge of physics of gas discharges (in our case, discharge that interacts with the solution), and the mechanism and kinetics of generation of active species (in liquid and gas phases) and their chemical reactions in solution. All these questions are as yet little understood, although the studies of chemical effects initiated by the simplest plasma – solution system, namely, a glow discharge with the electrolyte that plays the role of the electrode, date back to nearly 100 years ago. Güntherschulze (*e.g.*, see Ref. 2) studied the electroforming of aluminium and tantalum electrodes in electrolytic cells with dilute electrolyte solutions ($Na_2B_4O_7 - HBO_3$ and $Na_2B_4O_7$) and observed that the anodic sparkling was accompanied by the gas evolution on the anode at a rate higher than the value calculated based on the Faraday law and also the appearance of hydrogen peroxide in the solution. A hypothesis was advanced according to which gases were formed in a region immediately adjacent to the discharge zone as a result of the four-body recombination of oxygen and hydrogen atoms delivered from the discharge zone. Fundamental cycles of studies were accomplished by schools of Klemenc [3–7] in Germany and Hickling [8–16] in England. Although the interpretation of their results has now substantially changed, these studies are still of interest, the more so that no such comprehensive systematic studies were carried out since that time and no exhaustive reviews on this subject are known.

A G Zakharov, A I Maksimov, Yu V Titova Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, 153045 Ivanovo, Russian Federation. Fax (7-4932) 33 62 37, tel. (7-4932) 33 62 59, e-mail: agz@isc-ras.ru (A G Zakharov), tel. (7-4932) 33 62 64, e-mail: aim@isc-ras.ru (A I Maksimov), jvt@isc-ras.ru (Yu V Titova)

Received 26 October 2006
Uspekhi Khimii **76** (3) 260 – 278 (2007); translated by T Ya Safonova

II. Plasma – solution systems

1. Specific features and types of plasma – solution systems

The interaction of a gas discharge with solutions can be realised in the following two ways:

(1) with a discharge that contacts the liquid and is generated between two electrodes located in the gas phase;

(2) with a discharge in which the electrolyte solution plays the role of one or both electrodes.

In both cases, the properties of the system and the achieved results substantially depend on whether we deal with a (quasi)stationary discharge or a high-voltage pulsed discharge. The present review is chiefly devoted to plasma – solution systems (PSS) with stationary discharges; however, the studies of pulsed PSS are also discussed.

The first-type processes resemble conventional heterogeneous plasma-chemical processes in which active species generated in plasma diffuse to the interface to initiate chemical reactions in the solution. In the second-type systems, the discharge current passes through the electrolyte, which substantially changes the properties of the plasma – liquid interface. In this case, plasma can be generated either in the original plasma-forming gas that contains solvent vapours or within a vapour blanket formed in the liquid phase due to the superheat instability. Figure 1 shows possible configurations of systems differing in the roles of the metal and electrolyte electrodes. The Figure also shows different orders of alternation of interfaces formed by metals, plasma and solutions in PSS of different types. A plasma – solution system can be distinguished from a classical electrochemical system by the presence of one or two plasma – solution interfaces. Note that the

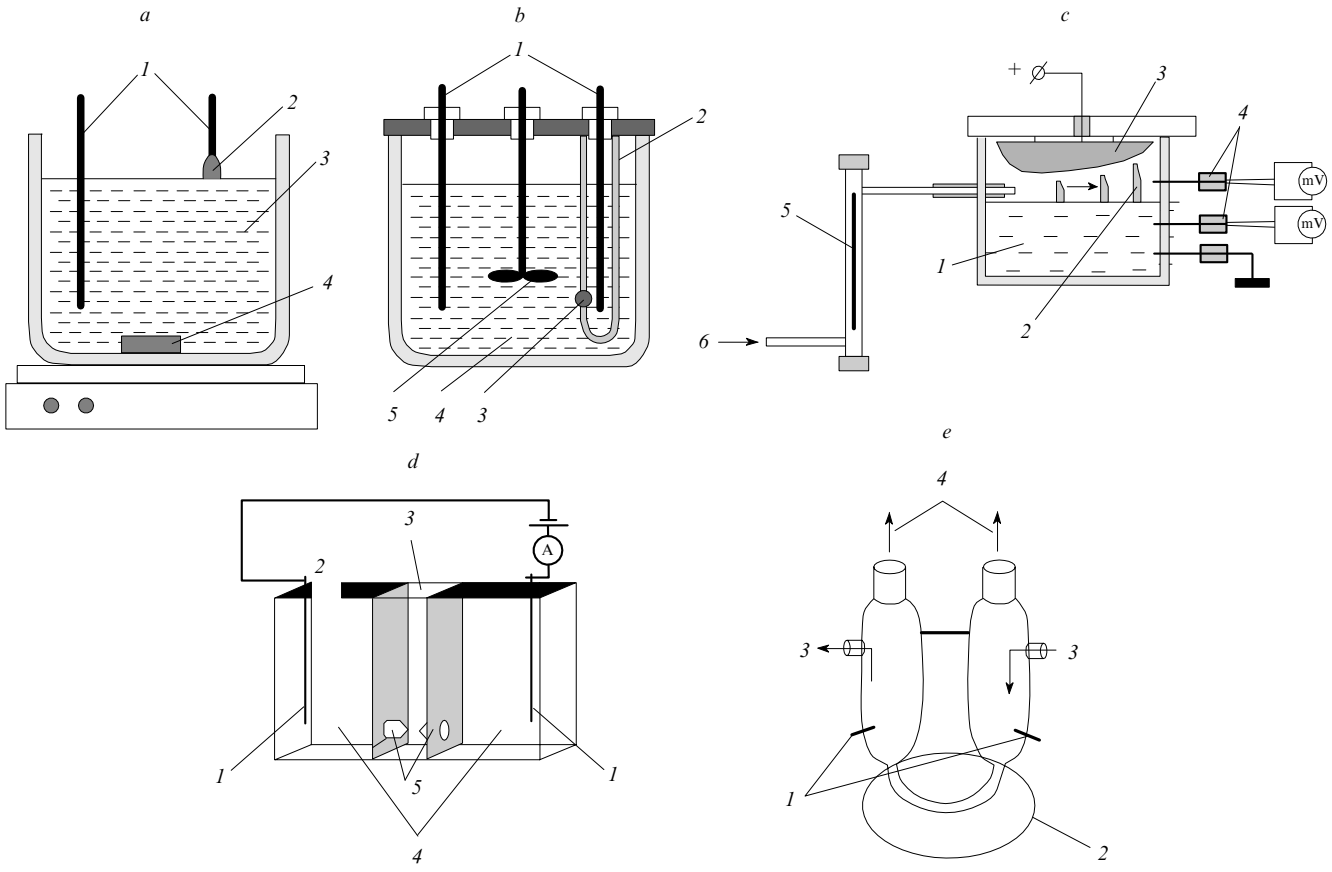


Figure 1. Configurations of discharge cells. In parentheses, the order of alternation of interfaces formed between metal (M), plasma (P) and electrolyte solution (E) is shown.
(*a*) Glow-discharge cell (M – E – P – M): (*1*) electrodes, (*2*) plasma zone, (*3*) electrolyte, (*4*) magnetic stirrer.
(*b*) Diaphragm discharge cell (M – E – P – E – M): (*1*) electrodes, (*2*) quartz ampoule, (*3*) diaphragm (plasma zone), (*4*) electrolyte, (*5*) stirrer.
(*c*) Gliding arc discharge cell (M – E – P – M): (*1*) solution, (*2*) gliding arc discharge, (*3*) special-shape electrode (anode), (*4*) thermocouple entry, (*5*) flow meter, (*6*) gas inlet.
(*d*) Diaphragm discharge cell with buffer compartments (M – E – P – E – M): (*1*) electrodes, (*2*) plasma zone, (*3*) active zone, (*4*) buffer compartments, (*5*) quartz ampoules with diaphragms.
(*e*) Cell for initiation of volume discharges in a tube filled with a solution (M – E – P – E – P – E – M): (*1*) electrodes, (*2*) discharge zone, (*3*) circulation of electrolyte solution, (*4*) to a reflux condenser.

plasma structures in these systems may be in direct contact with neither metal electrodes nor the external atmosphere.

The glow discharge in which the electrolyte solution serves as one of the electrodes (most often, the cathode) was studied most thoroughly (see Fig. 1*a*).[3–16] Apparently, anodic microdischarges that arise as a result of the breakdown of the oxide film on the surface of such metals as Al, Ta, Nb, which are immersed into the solution, can also be assigned to the same type.[17–22] Special mention should be made of PSS in which the plasma formed in the solution has a sufficiently large volume, which allows one to treat materials by combining the impacts of plasma and the plasma-activated solution (see Fig. 1 *e*).[23]

From out viewpoint, any strict classification of plasma – solution systems is hardly possible to date. A classification based on the analysis of the number of metal – solution and plasma – solution interfaces and the order of their alternation was proposed.[24] It is the dynamic plasma – solution interface that is the key feature of any PSS. Few available experimental data characterising this interface were obtained only for a glow discharge with electrolyte electrodes and exclusively for the case where the electrolyte serves as the cathode. For nonstationary continuous discharges, *e.g.*, diaphragm discharge, such studies are more cumbersome and are virtually unknown to date According to our viewpoint, the most important properties of the dynamic plasma – solution interface are similar for the mentioned discharge types. This is why below we consider only the glow discharge with the electrolyte as the cathode.

Drawing the analogy between a glow discharge with the electrolyte cathode and a classical low-pressure glow discharge, it should be noted that the cathodic potential drop at the electrolyte surface is determined by two characteristics, namely, the coefficient of electron emission from the solution (γ) and the Townsend coefficient of volume ionisation (α).[24] Measurements gave the cathodic potential drop at the electrolyte surface in the range from 300 to 800 V.[25] These values substantially exceed the usual cathodic potential drops obtained for glow discharges with metal electrodes, which apparently can be associated with the low coefficient γ. Estimates, which were based on an assumption that at low discharge currents (not exceeding tens of mA), the glow discharge with an electrolyte cathode can be considered as a conventional glow discharge, gave the values $\gamma = 10^{-4}-10^{-3}$ (Ref. 26).

The high potential drop at the surface of electrolyte cathodes determines the sufficiently high yields of primary active species in the thin surface layer of the solution. To our knowledge, the energy distribution of ions bombarding the

solution surface is yet unknown. However, it is evident that the maximum possible energy should correspond to the potential drop at the cathode surface.

Ionic bombardment of the solution surface not only leads to its effective chemical activation but also gives rise to an effect similar to the classical cathode sputtering, *i.e.*, the transfer of solution components into the plasma zone. According to the results of measurements,[27,28] the transfer coefficient of solvent (water) molecules, which is determined as the number of water molecules knocked out from the solution per incident ion exceeds 10^2; the transfer coefficient of the solute is approximately proportional to its mole fraction in the solution. The vapour jet that arises as a result of cathodic sputtering has a linear velocity of 50 – 100 cm s^{-1}. The energy consumed in its formation reaches 50% of the total discharge energy.[29] Estimates of average energy consumed in the transfer of a single water molecule to the plasma zone correspond to $\sim$50 kJ mol^{-1}, which does not differ much from the thermodynamically equilibrium consumption (43.3 kJ mol^{-1} at 40 °C [30]).

The presence of non-equilibrium vapour jet leads to the fact that regardless of the nature of the main plasma-forming gas, the ionisation of water molecules plays the key role in the formation of plasma; moreover, according to certain estimates,[25] the main ions in the plasma zone are $H_3O^+ \cdot H_2O$. The role played by this jet in the discharge-initiated processes in solution is of no less importance. The analysis of the mechanism of these processes requires taking into account the ion-bombardment-induced transfer of reagents and products into the gas zone.[31] The fact that recombination processes that involve primary active species ($HO^\bullet$, $H^\bullet$, e^-_{solv}) almost exclusively occur in the cathodic spot zone necessitates the separate consideration of the rates of processes initiated by primary species in the cathodic spot and those initiated by secondary species (*e.g.*, hydrogen peroxide) in the rest solution volume.[31]

2. The mechanism of chemical activation of solutions in plasma – solution systems

Despite the substantial difference in the PSS mentioned above, the main reason for the plasma activation of solutions is their bombardment with ions accelerated near the solution surface in the vicinity of the near-electrode (mainly cathodic) potential drop. This causes non-equilibrium dissociation and ionisation of, first of all, solvent molecules. As a result, $H^\bullet$, $HO^\bullet$ radicals and solvated electrons appear in the solution. This mechanism of activation followed by chemical reactions is close to that comprehensively studied in radiation chemistry.[32] The yields of primary active species depend on the cathodic potential drop formed. Another important effect of ionic bombardment is the transfer of solution components into the plasma zone. The data on its kinetics under the conditions of an atmospheric-pressure glow discharge are available.[26–28] Undoubtedly, the transfer processes initiated by ionic bombardment substantially affect the properties of other non-stationary PSS, including the migration of plasma wisps in solution. In the case of non-stationary discharges (diaphragm and volume discharges), a shock wave is initiated in the electrolyte bulk, the propagation of which can also affect the chemical processes in the solution.[33,34]

The contact of the plasma zone with the solution surface apparently activates the solution *via* the 'dissolution' of active species formed in the plasma by fairly well known mechanisms. However, the quantitative contribution of this activation mechanism to the observed yields of chemical reaction products in solutions still remains unclear. Obviously, this contribution can be higher when the plasma zone is located within the solution as in the case of anodic microdischarges or a diaphragm discharge.

3. Yields of primary active species in plasma – solution systems

Within the framework of the simplified scheme described above in the absence of discharge-initiated chain reactions in solutions, the yields of final products of redox reactions cannot exceed the yields of primary active species. Experimental results that allow one to directly check this assumption are scarce. Thus it was found [8,9,13,14] that with an increase in the salt concentration, the yields of oxidation products of Fe^{2+} and Ce^{3+} approach the yields of $HO^\bullet$ radicals found in the same studies. As a whole, these results do not contradict the above assumption. The only exclusion was the far too high yield observed [35] in the oxidation of Fe^{2+} to Fe^{3+} with a very low discharge current (0.1 mA). Table 1 shows the discussed results.

III. The effect of gas discharges on physicochemical properties of solutions

Initiation of redox reactions in solutions should be accompanied by the changes in their acidity. At the same time, the observed pH changes sometimes cannot be explained by this effect. As demonstrated for a corona discharge [43] and, later, for a gliding arc discharge burning between two metal electrodes in the immediate vicinity of the solution surface,[44] the pH of aqueous solutions in contact with a gas discharge decreased. In both studies, the discharge-activated gas was in contact with the aqueous solution surface but no discharge current passed through the solution. Moreover, according to the authors of these studies, the effect of a powerful gliding arc discharge on the solution pH completely resembled the titration of a strong alkali with a strong acid (*i.e.*, the pH changes were sharp and great). The simplest explanation of this effect assumes the formation of nitrogen oxides in the plasma zone followed by their dissolution.

In the studies of the effect of a glow discharge on the acidity of solutions of alkali metal chlorides,[26] no oxidation processes initiated in the liquid phase were found; however, in dilute solutions, a strong and steady decrease in the pH was observed, where the changes in the proton concentration in solution corresponded to the quantity of electricity passed. In was assumed [45] that the observed effect can be attributed to a redox process initiated by ion bombardment and localised in the gas phase. This process gave alkali metal atoms and chlorine molecules observed experimentally in the gas phase. Under the experimental conditions used, virtually no sodium returned to the liquid phase, in contrast to chloride. Thus, in this case, the changes in the solution acidity were determined by the transfer rate of the solute to the gas phase under the action of ion bombardment.

The changes in the acidity of solutions subjected to a gas discharge were accompanied by the changes in the solution conductivity.[46] The conductivity of concentrated acids and alkalis subjected to a diaphragm discharge decreased, whereas the conductivity of salt solutions remained unchanged.[47] Taking into account the mechanisms of conduction in these solutions, this effect was explained by the changes in the structural characteristics of acid and alkali solutions, which affected the effectiveness of the relay mechanism of charge transfer in them.

Table 1. Yields of the primary active species or the products of redox processes initiated by these species.

Species or process	Yield /mol F^{-1} (see [a])	Conditions	Ref.
$HO^{\bullet}$, $H^{\bullet}$	7.3	glow discharge (25 – 125 Torr), $FeSO_4$ solution	9
	7.6	glow discharge (25 – 125 Torr), $Ce_2(SO_4)_3$ solution	10
	8.3	glow discharge (25 – 125 Torr), NaN_3 solution	10
	3.16 – 3.58	microdischarges in aqueous solution of $NH_3 + H_3BO_3$	18
e^-_{solv}	3.3	glow discharge, sulfuric acid solution	3
	6.0 ± 0.6	solutions of salts of chloroacetic acid	17
H_2O_2	0.532	low-pressure glow discharge, current 60 mA, 1 M H_2SO_4	4
	1.1 – 1.9	glow discharge (75 – 100 Torr), current 50 – 100 mA, pH 1 – 8	8
	0.66 – 1.1	contact discharge (1 atm), sulfate buffer	36
	0.42	glow discharge (750 Torr), current 25 mA, 0.49 M NH_3 (aq.)	37
	3.39	glow discharge (100 Torr), phosphate buffer with addition of 0.9 mol $litre^{-1}$ ethanol, bubbling of O_2 through the solution (900 $cm^3\ s^{-1}$), current 30 mA	38
	0.64 – 9.75	glow discharge (1 atm), 0.01 – 0.5 M Na_2SO_4, KCl, KOH, current 8 – 30 mA	39
$I^- \longrightarrow I_2$	0.18 – 2.88	glow discharge (1 atm), current 6 mA, 0.15 – 0.25 M KI	29
	3.2	glow discharge, 0.02 M KI, neutral phosphate buffer (the maximum yield is shown)	40
$Fe^{2+} \longrightarrow Fe^{3+}$	7.3	glow discharge (50, 75, 100 Torr), current 25 – 100 mA, 0.005 – 0.075 M $FeSO_4$ (the limiting yield reached at the maximum salt concentration is shown)	9, 10
	11; 25	glow discharge in air (25 Torr), current 4.2 or 0.1 mA, 0.01 M iron ammonium sulfate solution in 0.5 M H_2SO_4	35
$Ce^{3+} \longrightarrow Ce^{4+}$	7.6	glow discharge (50, 75, 100 Torr), currents 25 – 100 mA, 0.005 – 0.075 M $Ce_2(SO_4)_3$ (the limiting yield reached at the maximum salt concentration is shown)	9, 10
$K_4[Fe(CN)_6] \longrightarrow K_3[Fe(CN)_6]$	7.3	glow discharge in air, nitrogen, oxygen (50 Torr), currents 75 mA (limiting yields reached at the increase in the salt concentration to 0.45 mol $litre^{-1}$ are shown)	41
	5.7	glow discharge in hydrogen (50 Torr), current 75 mA (limiting yields reached at the increase in the salt concentration to 0.45 mol $litre^{-1}$ are shown)	41
	0.5 – 0.9	atmospheric-pressure glow discharge, current 5 or 10 mA, $K_4[Fe(CN)_6]$ concentrations $1 \times 10^{-3} - 5 \times 10^{-2}$ mol $litre^{-1}$	42
$KMnO_4 \longrightarrow MnO_2$	1.25	atmospheric-pressure glow discharge in air, current 20 mA	29
	0.66	atmospheric-pressure gliding arc discharge in air, current 20 mA	29

[a] From hereon, F corresponds to Faraday, *i.e.*, an off-system unit widely used in electrochemistry, namely, $1\ F \approx 9.65 \times 10^4$ C.

IV. Plasma-initiated chemical processes in solution

Table 2 shows examples of redox processes that occur in solution under the action of gas discharges.

Table 2. Examples of redox processes initiated by gas discharge in aqueous electrolyte solutions.

Reaction	Medium
Oxidation reactions	
$I^- \longrightarrow I_2 \longrightarrow IO_4^-$	neutral, acidic
$Br^- \longrightarrow Br_2 \longrightarrow BrO_4^-$	the same
$S^{2-} \longrightarrow S \longrightarrow SO_3^{2-} \longrightarrow SO_4^{2-}$	"
$Cl^- \longrightarrow Cl_2 \longrightarrow ClO_2^-$	"
$Mn^{2+} \longrightarrow MnO_2$	"
$Cr^{3+} \longrightarrow Cr_2O_7^{2-}$	"
$Fe^{2+} \longrightarrow Fe^{3+}$	"
$[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-}$	neutral
$Ce^{3+} \longrightarrow Ce^{4+}$	acidic
$Tl^+ \longrightarrow Tl^{3+}$	the same
Reduction reactions	
$MnO_4^- \longrightarrow MnO_2$	neutral
$Cr_2O_7^{2-} \longrightarrow Cr_2O_3$	the same
$VO_3^- \longrightarrow VO^{2+}$	"

The number of studies devoted to chemical reactions in solutions initiated by different types of gas discharge is sufficiently large. However, the comprehensive analysis of all these data is complicated because the experimental conditions used were substantially different and often described in insufficient detail.

1. Hydrogen peroxide generation in electrolyte solutions subjected to the gas-discharge plasma

Klemenc *et al.*[3–6] pioneered the quantitative studies of the formation of hydrogen peroxide in PSS. Hickling *et al.*[8, 15] carried out further comprehensive investigations of the hydrogen peroxide formation in aqueous solutions subjected to a low-pressure discharge (50 – 75 Torr) with the anode located in the gas phase. According to their results, hydrogen peroxide was formed in an amount proportional to the quantity of electricity passed, the accumulation of hydrogen peroxide was accompanied by its decomposition, which ultimately led to its steady-state concentration. The amount of H_2O_2 formed in the solution upon the passage of a given charge through it was independent of both the current and the factors that determine the discharge nature and can be described by the following expression:

$$C_{eq} = \frac{F}{k}\left[1 - \exp\left(\frac{akq}{V}\right)\right],$$

where C_{eq} is the steady-state concentration of H_2O_2, F is the Faraday constant, k is the rate constant for the hydrogen peroxide decomposition, a is a numerical coefficient equal to 1.1 – 1.9 which corresponds to the number of hydrogen peroxide equivalents primarily formed per Faraday of electricity (the initial yield is G_0), q is the quantity of electricity in Faradays, V is the solution volume.

The process followed the same mechanism in the pH range from 1 to 9. However, beyond this range, the H_2O_2 yield decreased. In strongly alkaline solutions, no hydrogen peroxide was detected. Presumably, this can be associated with its anodic decomposition at the discharge of hydroxyl ions. The primary formation of hydroxyl radicals dimerisation of which yields peroxide was assumed to occur in the solution. At high concentrations, hydrogen peroxide decomposed in the reaction with the mentioned $HO^{\bullet}$ radical. The hydrogen peroxide yield was observed to depend relatively weakly on the electrolyte concentration (including aqueous ammonia and sulfuric acid solutions) and also on the nature of the primary plasma-forming gas and its pressure.[11–16]

Considering the formation of hydrogen peroxide as a result of dimerisation of $HO^{\bullet}$ radicals, one can expect the appearance of H_2O_2 in alcohol solutions. However, in the glow-discharge-treated solution of 0.3 M $LiClO_4$ in methanol, formaldehyde was the main product and no hydrogen peroxide was detected.[33] A totally different situation was observed upon plasma treatment of aqueous ethanol in the presence of oxygen.[38] The action of an anodic glow discharge on ethanol in its neutral aqueous solution (a phosphate buffer) afforded acetaldehyde, butane-2,3-diol and hydrogen peroxide. The yields of these products strongly depended on both the oxygen flow and stirring. With the increase in the discharge current, the maintenance of the hydrogen peroxide yield at a constant level requires the increase of the oxygen consumption. Under experimental conditions, the amount of formed H_2O_2 linearly increased with the increase in the quantity of electricity passed, *i.e.*, no discharge-induced decomposition of hydrogen peroxide took place.

Kinetic curves of hydrogen peroxide accumulation measured [8, 15, 40, 48] under different conditions were processed in our studies with the use of an exponential relationship similar to that proposed by Hickling [8, 15]

$$C = C_{\lim}\left[1 - \exp(-BQ)\right],$$

where C is the current concentration of hydrogen peroxide, $C_{\lim}$ is the maximum concentration of hydrogen peroxide obtained by using this processing procedure, B is the empirical coefficient, Q is the quantity of electricity passed through the system. Table 3 shows the obtained results.

Table 3. Kinetic characteristics of the hydrogen peroxide accumulation under different conditions.[a]

Experimental conditions	$10^3\,C_{\lim}$ /mol litre^{-1}	$10^3\,B$ /F^{-1}	υ (see [b]) /mol F^{-1}	Ref.
Contact discharge (1 atm), 0.05 M K_2SO_4	0.2	1.88	0.376	8
Glow discharge (50 Torr), current 75 mA, 0.4 M H_2SO_4	1.7	0.405	0.688	15
Glow discharge (50 Torr), current 110 mA, 0.05 M $NaHSO_4$	2	0.403	0.806	40
Contact discharge (1 atm), current 110 mA, 0.02 M H_2SO_4	10	0.189	1.89	48

[a] Initial current yield of H_2O_2 were practically the same ($\sim$1.5 mol F^{-1}); [b] υ is the formation rate of H_2O_2.

For similar discharge currents, the initial current yields of hydrogen peroxide were virtually the same, whereas its limiting concentrations differed by more than an order of magnitude. Moreover, the maximum difference was observed for only one type of discharge, namely, the contact discharge, *i.e.*, the explanation should be sought in the discharge as such. This means that even for the same discharge type, the rates of discharge-induced hydrogen peroxide decomposition can differ by two orders of magnitude.

In the aforementioned studies, Hickling also examined the decomposition of hydrogen peroxide for the cases where 0.05 M solutions of H_2SO_4, Na_2HPO_4 and NaOH with different starting H_2O_2 concentrations were subjected to the discharge. It was found that in discharge-treated sulfuric acid and sodium phosphate solutions, the amount of hydrogen peroxide changed until its steady-state concentrations corresponding to those found in experiments on the peroxide synthesis were reached. In the alkaline solution, decomposition of hydrogen peroxide with the current efficiency equal to 1 persisted, which was explained by the following anodic processes:

$$HO^- - e^- \longrightarrow HO^{\bullet},$$

$$HO^{\bullet} + H_2O_2 \longrightarrow H_2O + HO_2^{\bullet},$$

$$HO^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O + O_2.$$

2. Oxidation processes initiated by a gas discharge in aqueous solutions of inorganic substances

A gas discharge initiates both oxidation and reduction reactions in solution (see Table 2). According to available data, the discharge initiates all thermodynamically permissible redox reactions that involve primary active $HO^{\bullet}$ species. At the same time, the rate of the process strongly depends on the ratio of redox potentials of the corresponding half-reactions.

The oxidation of $FeSO_4$, NaN_3 and $Ce_2(SO_4)_3$ initiated by a glow discharge at reduced pressure (125 – 250 Torr) in the argon atmosphere was studied.[9, 10, 13, 14, 35, 44]

It was found [9] that the yield of oxidation products of $FeSO_4$ (G /equiv F^{-1}) can be described by the relationship

$$G = 1 + n\frac{[Fe^{2+}] + A}{[Fe^{2+}] + A + B},$$

where n is the number of equivalents of the oxidant, which were formed per Faraday of electricity, A and B are empirical constants.

Presumably, the majority of obtained experimental results can be explained based on the assumption that the $HO^{\bullet}$ radical is the primary oxidation agent. The kinetic model, which was developed based on the experimental data, has led to a relationship similar to that shown above and allowed the empirical kinetic characteristics for the oxidation of three substrates mentioned above to be found. The initial yield of $HO^{\bullet}$ (mol F^{-1}) was determined to be 7.3 for iron sulfate, 7.6 for cerium sulfate and 8.3 for sodium azide (the limiting yields obtained at the maximum salt concentration are shown).[9, 10]

Glow-discharge-induced oxidation of $K_4[Fe(CN)_6]$ was studied.[41] With the increase in the concentration of oxidised ions, the yield of oxidation products tended to a limit of 7 mol F^{-1} (at the salt concentration of 0.45 mol litre^{-1}). Presumably, the main oxidation reactions were as follows:

$$HO^{\bullet} + Fe(CN)_6^{4-} \longrightarrow Fe(CN)_6^{3-} + HO^-,$$

$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet},$$

$$HO_2^{\bullet} + Fe(CN)_6^{4-} \longrightarrow HO_2^- + Fe(CN)_6^{3-}.$$

The reduction of $K_3[Fe(CN)_6]$ under the action of hydrogen atoms was neglected.

The oxidation of $K_4[Fe(CN)_6]$ to $K_3[Fe(CN)_6]$ initiated by a 'positive' atmospheric-pressure glow discharge between an electrode-tip in the gas phase and the surface of an aqueous electrolyte solution was studied[42] as a function of the gas discharge current and the concentration of the starting compound. The currents of 5 and 10 mA were used, the voltage at electrodes did not exceed 5 kV. Table 4 shows the results obtained.

Table 4. Initial oxidation rates (υ_0) of potassium hexacyanoferrate(II) and current yields (G) for different discharge conditions.[42]

Discharge current /mA	$10^3 C_0$ /mol litre^{-1} (see [a])	$10^7 \upsilon_0$ /mol litre^{-1} s^{-1}	G [b]
10	5	2.27	0.88
	2	1.91	0.74
	1	1.99	0.77
	0.5	2.34	0.90
	0.25	2.45	0.94
5	0.5	0.904	0.70
	0.25	0.728	0.56
	1	0.683	0.53

[a] C_0 is initial concentration of $K_4[Fe(CN)_6]$.
[b] Average current yield is expressed as the number of $K_3[Fe(CN)_6]$ molecules formed per incident ion.

The oxidation of ammonium ions under the discharge conditions was studied.[37] Air-saturated stirred aqueous ammonia (50 ml) served as the working solution. In the 'positive' discharge, the main products were hydrogen peroxide, hydrazine, hydroxylamine and nitrite ions. In the 'negative' discharge, neither hydrogen peroxide nor hydrazine were detected. In both cases, no formation of nitrate ions was observed. Both anodic and cathodic discharges afforded nitrogen and hydrogen as the gaseous products. In a cooled trap behind the discharge cell, only NH_3 and H_2O were detected.

Sulfuric acid oxidation was studied back in the work by Klemenc and Eder.[4] They have found that the oxidation products of sulfuric acid under the action of a glow discharge were (in addition to hydrogen peroxide) peroxydisulfuric ($H_2S_2O_8$) and peroxymonosulfuric (H_2SO_5) acids. The effect of minor additives on this process was studied[5] (see below). Denaro and Hough[48] studied the oxidation of sulfuric acid under a glow discharge in 0.4 M H_2SO_4 under a nitrogen atmosphere, at a pressure of 50 Torr and a discharge current of 57 mA. The authors observed the formation of the same products; however, according to their data, hydrogen peroxide was produced in the highest yield, whereas the yield of peroxydisulfuric acid was very low. The total yield of oxidation products, which was assumed equal to the sum of yields of hydrogen peroxide and peroxydisulfuric acid was found as well as individual yields of each product mentioned. Figure 2 shows the dependence of the overall concentration of oxidation products on the quantity of electricity passed.

The following reactions that lead to the formation of oxidation products were considered:[48]

$$H_2O \longrightarrow H^{\bullet} + HO^{\bullet} \text{ (reaction rate } R_i),$$
$$HO^{\bullet} + HSO_4^- \xrightarrow{k_1} HSO_4^{\bullet} + HO^-,$$
$$HO^{\bullet} + HO^{\bullet} \xrightarrow{k_2} H_2O_2,$$
$$HO^{\bullet} + H^{\bullet} \xrightarrow{k_3} H_2O,$$
$$H^{\bullet} + H^{\bullet} \longrightarrow H_2,$$

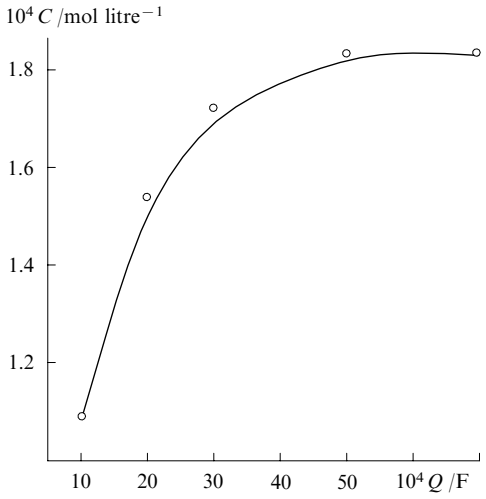


Figure 2. Dependence of the overall concentration (C) of sulfuric acid oxidation products ($H_2SO_5 + H_2O_2$) under a glow discharge on the quantity of electricity (Q) passed.

$$H^{\bullet} + HSO_4^{\bullet} \longrightarrow H_2SO_4,$$
$$HO^{\bullet} + HSO_4^{\bullet} \longrightarrow H_2SO_5.$$

Using the values of rate constants $k_1 \approx 8 \times 10^5$, $k_2 = 1 \times 10^{10}$, $k_3 = 3.2 \times 10^{10}$ litre mol^{-1} s^{-1} and assuming that the thickness of the active layer at the cathodic spot was $\sim$1 nm, the authors assessed the rate (R_i) of generation of radicals and their concentrations to be $R_i = 261$ mol litre^{-1} s^{-1}, $[HO^{\bullet}] = 8.17 \times 10^{-5}$, $[H^{\bullet}] = 6 \times 10^{-5}$ mol litre^{-1} (the latter quantity pertains to the primary reaction zone with a thickness of $\sim$400 nm).

Oxidation of potassium iodide solutions was also studied.[40] The effect of a glow discharge on acidic and neutral KI solutions in hydrogen atmosphere was explored. Solutions were prepared from 0.4 M H_2SO_4 and a neutral phosphate buffer (0.1 M Na_2HPO_4 + 0.1 M KH_2PO_4). The formation of molecular iodine and hydrogen peroxide was expected. Hydrogen peroxide complicated the analysis because it could react both during the discharge and after its quenching. To solve this problem, 1 ml of 20% ammonium molybdate solution was added to the cell as the catalyst of the hydrogen peroxide reaction with iodide ions. Under these conditions, I_2 was expected to become the only product of this process. Figure 3 shows the measured total yields of oxidation products. In contrast to other cases [oxidation of bivalent iron, potassium hexacyanoferrate(II), *etc.*], the dependences of the yield of oxidation products passed through the maximum rather than tended to a limit.

Oxidation of potassium iodide subjected to a gliding arc discharge was studied.[44] For a discharge power of 1 kW dissipated in 50 ml of solution, the steady-state concentration of oxidation products was attained in $\sim$1 h.

Spectrophotometric studies[29,49–51] were devoted to the oxidation of iodide ions under a glow discharge. The changes in the absorption of a neutral potassium iodide solution subjected to a stationary discharge were studied at a wavelength of 460 nm for different starting concentrations. During the plasma treatment, the optical density of the solution passed through a maximum the height and position of which strongly depended on the starting concentration of iodide ions. The initial segments of optical density curves were almost linear. The curves' segments at greater times described the optical density to descend by approximately the exponential law.

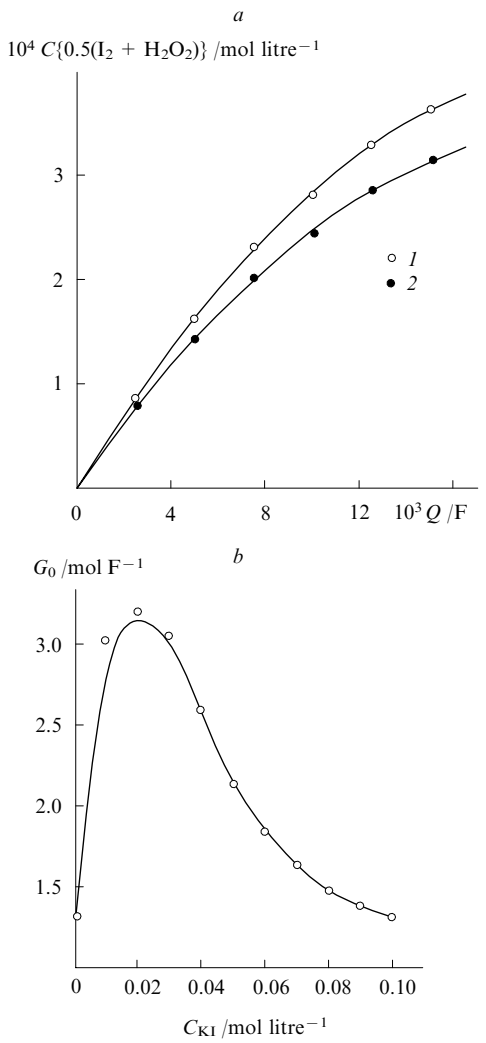


Figure 3. Dependences (*a*) of the overall concentration of KI oxidation products under the action of a glow discharge on the quantity of electricity passed through the solution and (*b*) of the initial current efficiency on the KI concentration in solution. Hydrogen atmosphere (50 Torr), current 75 mA.
(*1*) Acidic medium, (*2*) alkaline medium.

Table 5 shows the characteristics of gas-discharge-initiated oxidation of iodide ions calculated from experimental results.

Due to a high rate of the transformation of molecular iodine to triiodide ions,[52] the initial segments of absorption curves measured at moderate starting concentrations of iodide ions directly illustrated the accumulation of triiodide ions. This conclusion was confirmed by the absorption spectra of KI solutions treated in plasma. At short treatment times, merely the absorption of triiodide ions was observed, which monotonically increased with an increase in the exposure time. Experiments at low starting concentrations of iodide ions showed that the optical density of solutions descended for the greater doses of treatment, *i.e.*, the formation of polyiodide ions was merely the first stage of oxidation. Qualitative chemical analysis of solutions thus treated indicated the formation of iodates.

Table 5. Oxidation rates (υ) of iodide ions and current yields (G_0) of the oxidation product (stationary glow discharge, discharge current 6 mA).[29]

$10^3\ C_0$(KI) /mol litre^{-1}	$10^7\ \upsilon$ /mol litre^{-1} s^{-1}	G_0 /mol F^{-1}
0.9	1.57	0.45
1.8	0.63	0.18
3.6	1.38	0.4
7.23	9.8	2.88
15	3.4	0.96

Studies of the effect of plasma formed in a stationary glow discharge and a gliding arc discharge on aqueous solutions of sodium sulfide have shown [29] that plasma-initiated oxidation of sulfide ions proceeds *via* sulfur and polysulfide ions to ultimately afford sulfites and sulfates. These conclusions were drawn based on spectral measurements and the qualitative chemical analysis of treated solutions.

3. Reduction of inorganic compounds

Plasma-initiated reduction reactions in solutions were far less studied as compared with oxidation reactions. Early studies by Klemenc [3, 4] provided the most systematic data. The precipitation of metal or metal oxide from salt solutions and the reduction of certain acids ($HClO_3$, $HBrO_3$, $HClO_4$, HNO_3, *etc.*) were investigated.[3]

The reduction of potassium chlorate in a neutral solution yielded chloride ions. The reduction of $KBrO_3$ proceeded quite efficiently even in neutral solutions (like the reduction of chlorates in acidic solutions). Chromic acid was reduced almost completely to a chromium(III) salt. Perchloric acid failed to be reduced in the conventional electrolysis. A glow discharge initiated its reduction with the conversion degree dependent on the concentration. Table 6 compares the reduction processes that occur in the classical electrolysis and with the plasma activation.

The studies [4] of the reduction of perchloric and chloric acids and their salts have revealed the following specific features.

1. The discharge-induced reduction of perchloric and chloric acids and their salts can occur with either anode or cathode located in the gas phase.

2. The reduction of perchloric acid in the region of the cathodic potential drop (when the anode is located in the gas

Table 6. Features of reduction under conditions of classical electrolysis and glow discharge.[3]

Electrolyte	Classical electrolysis	Glow discharge [a]	Notes
KNO_3	the products are NH_3 and NH_2OH	the products are HNO_2, NO and N_2O	alkaline solution
$Fe_2(SO_4)_3$	easily reduced	reduced insignificantly	sulfuric acid solution
$KClO_3$	no or insignificant reduction on a Cu – Pt electrode,	reduction (12%)	neutral solution
	substantial reduction on a Fe electrode	reduction (90%)	acidic solution
$KBrO_3$	readily reduced on a Pt electrode	reduction (90%)	neutral or acidic solution
H_2CrO_4	reduction to $Cr_2(CrO_4)_3$	reduction (88%)	–
$HClO_4$	no reduction	stepwise reduction (up to 40%)	Cu or Pt electrode

[a] In parentheses, the yield of reduction products is shown.

Table 7. Reduction of perchloric and chloric acids and their salts under conditions of classical electrolysis in a glow discharge.[4]

Electrolyte	Classical electrolysis	Reduction in a glow discharge (%)	
		cathode in the gas phase	anode in the gas phase
$HClO_3$, 1 M	insignificant reduction on a Pt electrode	500	2600
$HClO_4$, 1 M	is not reduced on a Cu – Pt electrode	20	200
$KClO_3$, 0.26 M	insignificant reduction on conventional electrodes	90	500
$NaClO_4$, 0.5 M	is not reduced on a Pt electrode	insignificant reduction	60
	insignificant reduction on a Ni – Fe electrode	the same	no noticeable reduction

phase) demonstrates the strongest (40-fold in 2.5 M solution) increase in the yield of products over the faradaic yields.

3. The reduction of perchloric acid corresponds to its decomposition to HCl and O_2.

4. Side reactions that produce detonating gas occur at a rate, which is the higher the slower the corresponding reduction reaction in the electrolyte.

5. The ratio of current efficiencies observed in the anodic and cathodic compartments is the same for the oxidation of sulfuric acid solutions and the reduction of perchloric acid.

Table 7 compares the reduction processes that occur in the classical electrolysis with the corresponding plasma-electrolytic reactions.

The reduction of inorganic ions under the action of a stationary glow discharge at atmospheric pressure was studied [53, 54] (the discharge current was 10 mA, the solution volume was 400 ml). The following processes were observed:

$$MnO_4^- \longrightarrow MnO_2 \longrightarrow Mn^{2+} \text{ (neutral medium)},$$

$$MnO_4^- \longrightarrow MnO_4^{2-} \longrightarrow MnO_2 \text{ (alkaline medium)},$$

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+},$$

$$IO_3^- \longrightarrow I_2 \longrightarrow I^-.$$

4. Gas evolution processes

In 'classical' electrolysis of aqueous electrolyte solutions, the evolution of main gaseous products (oxygen and hydrogen) is associated with the electrode processes of the discharge of hydroxyl and hydronium ions. The situation changes crucially when the electrode represents the plasma in contact with a solution. Ions accelerated in the region of the potential drop at the solution surface initiate dissociation of solvent molecules. This gives rise to many effects including the evolution of gaseous products, which does not obey the Faraday law. At the same time, ions that came to solution from the plasma zone and underwent thermalisation can either be solvated or recombine with solution counter-ions, which ultimately affords gaseous products in yields corresponding to the Faraday law. Hence, the analysis of the gas evolution in the course of the plasma treatment of solutions might shed light on the behaviour of ions injected into the solution from the plasma zone and answer the question on the role of their solvation.

It was noted [5] that, if exclude the secondary effects, the gas evolution was never observed in the cathodic spot region on the solution surface. This makes the bulk recombination of ions injected into the plasma zone quite unlikely.

It was shown [7] that in addition to the faradaic ('polar', according to the authors of Ref. 7) gas evolution, the electrolysis in a glow discharge always produces the detonating gas. The cathodic spot is the source of active species that lead to the formation of the latter gas. The amount of evolved detonating gas can be many times increased if one surrounds the cathodic spot with a narrow glass cylinder. The effect manifests itself to the full extent only if the cylinder is completely immersed into the electrolyte. Based on these experiments, it was concluded [5] that the 'non-polar' formation of detonating gas occurs only as a result of a heterogeneous process.

The formation of oxygen and hydrogen in the anodic and cathodic discharges was studied.[12] A solution of 0.05 M K_2SO_4 served as the electrolyte. Figure 4 shows the dependences of the oxygen and hydrogen yields on the quantity of electricity passed through the solution and the potential drop in the discharge gap for a 'positive' contact discharge. As seen from the Figure, the processes that do not obey the Faraday law make the main contribution to the formation of gaseous products. In a 'negative' contact discharge, the yields of oxygen (1.84 mol F^{-1}) and hydrogen (2.73 mol F^{-1}) also substantially exceeded their faradaic yields.

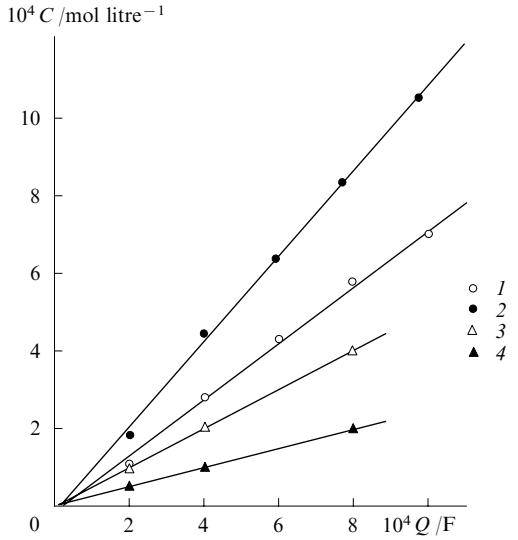


Figure 4. Dependences of (*1*) oxygen and (*2*) hydrogen yields on the quantity of electricity passed under the action of a glow discharge on a K_2SO_4 solution; (*3*) and (*4*) corresponding 'faradaic' yields.

5. Oxidation processes initiated by a glow discharge in solutions of organic compounds

a. Oxidation of alcohols

The effect of a glow discharge on a methanol solution was studied.[38] In the cathodic glow discharge, the main products were formaldehyde and formic acid. The anodic discharge produced fomadehyde and insignificant amounts ($\sim 1\%$ of the HCOH yield) of formic acid, ethylene glycol and dimethoxymethane. No hydrogen peroxide formation was observed. In both cathodic and anodic discharges, hydrogen, methane and carbon monoxide were the main gaseous products. Trace amounts of ethane, ethylene and acetylene were detected.

The medium becomes acidic under the action of a 'positive' discharge and alkaline when subjected to a 'negative' discharge.

The effect of a glow discharge on the ethanol solution was considered in the same publication. Oxygen and argon at a pressure of 100 Torr served as the working gas. The main

reaction products included acetaldehyde, hydrogen peroxide and butane-2,3-diol. Their yields strongly depended on the presence of oxygen in this system and the intensity of its flow. The other key factors were the gas pressure, the intensity of stirring, the discharge current and the quantity of electricity passed. The hydrogen peroxide yield increased with an increase in the oxygen flow rate. The following mechanism of the processes was put forward. In the absence of oxygen and at a sufficient concentration of ethanol, the main initial reaction was the capture of hydroxyl radicals by ethanol molecules. The reactions of hydrogen atoms and solvated electrons proceeded more slowly. The reaction of $H^{\bullet}$ and $HO^{\bullet}$ radicals with ethanol is sufficiently well studied. A $HO^{\bullet}$ radical abstracts a hydrogen atom from an ethanol molecule to form the following products: $CH_3CH_2O^{\bullet}$ (2.5%), $CH_3CHOH^{\bullet}$ (84.3%), $CH_2CH_2OH^{\bullet}$ (13.2%). The rate of the reaction of hydrogen atoms with ethanol molecules was lower by approximately two orders of magnitude. The main process was the elimination of a hydrogen atom from the CH_2 group to afford molecular hydrogen and a $CH_3CHOH^{\bullet}$ radical. In turn, radicals $CH_3CH_2O^{\bullet}$ and $CH_2CH_2OH^{\bullet}$ abstracted a hydrogen atom from an ethanol molecule. In the second case, this led to the conversion of the $HO^{\bullet}$ radical into the 1-hydroxyethyl radical.

The action of a glow discharge on a water – ethanol solution of a neutral phosphate buffer under the argon atmosphere produced hydrogen peroxide, butanediol and acetaldehyde.[38]

$$HO^{\bullet} + HO^{\bullet} \longrightarrow H_2O_2,$$

$$2\,CH_3CHOH^{\bullet} \longrightarrow CH_3CH(OH)CH(OH)CH_3,$$

$$2\,CH_3CHOH^{\bullet} \longrightarrow CH_3CHO + CH_3CH_2OH.$$

The following solvated electron reactions were considered:

$$e^-_{aq} + CH_3CHO \longrightarrow CH_3CHO^-,$$

$$CH_3CHO^- + H_2O \rightleftharpoons CH_3CHOH + HO^-,$$

$$e^-_{aq} + H_2O_2 \longrightarrow HO^{\bullet} + HO^-.$$

The hydroperoxyl radical $HO_2^{\bullet}$ played an important role in the discussed processes.

$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet},$$

$$e^-_{aq} + O_2 \longrightarrow O_2^-,$$

$$2\,HO_2^{\bullet} \longrightarrow O_2 + H_2O_2,$$

$$HO_2^{\bullet} + CH_3CO_2HOH^{\bullet} \longrightarrow CH_3CHO + H_2O_2 + O_2,$$

$$CH_3CO_2HOH^{\bullet} \longrightarrow CH_3CHO + HO_2^{\bullet},$$

$$2\,HO_2^{\bullet} \longrightarrow O_2 + H_2O_2.$$

Thus, the presence of oxygen in the system gives rise to two additional channels for the formation of hydrogen peroxide. One channel is associated with the intermediate formation of organic peroxyl radicals and the second corresponds to the formation of hydroperoxyl radicals.

Bugaenko *et al.*[21,55] studied the conversion of 0.1 – 3 M solutions of methanol and ethanol in a carbonate electrolyte under the action of microdischarges on an aluminium anode. Table 8 shows the main reaction products and their energy yields. The products of ethanol conversion were formed both within gas-vapour bubbles and in the near-surface liquid layer (the yield of the latter amounted to no more than 20% of the total yield).

The results shown above allow one to qualitatively compare the effects of a glow discharge (at reduced pressure) and anodic microdischarges on methanol and ethanol solutions. The reaction products for both PSS types by and large coincided. However, it should be mentioned that the reaction

Table 8. Energy yields of reaction products of 2 M ethanol and 2 M methanol in a 0.03 M solution of sodium carbonate under the action of microdischarges on an aluminium anode (voltage 500 V, current 90 mA, error of yield determination < 10%).[21,55]

Product	Yield /number of molecules per 100 eV	
	ethanol solution	methanol solution
H_2	1.90	2.60
CO	0.72	1.30
CH_4	0.29	0.27
C_2H_6	0.17	–
C_2H_4	0.40	–
$C_2H_6 + C_2H_4$	–	0.11
C_3H_8	0.056	0.0086
$C_2H_2 + C_3H_6$	0.19	0.010
C_4H_{10}	0.13	–
CH_3OH	0.030	–
$CH_3CH(OH)CH_2OH$	0.015	–
$CH_3CH(OH)CH(OH)CH_3$	0.015	–
CH_2O	0.041	0.28
$(CH_2OH)_2$	–	0.098
HCOOH	–	0.058
CH_3CHO	0.260	–
CH_3COOH	0.050	–
H_2O_2	0	0

Note. The consumption of ethanol and methanol (calculated from the yields of products) was 1.83 and 2.38 molecules per 100 eV of energy, respectively.

products formed under the action of a glow discharge on a methanolic solution of $LiClO_4$ included dimethoxymethane, which was absent when methanol in aqueous sodium carbonate solutions was subjected to anodic microdischarges. The quantitative comparison of yields of products in these PSS is complicated by the fact that the yields are expressed in different units, namely, per 100 eV of consumed energy (anodic microdischarges) and in mol F^{-1} (glow discharge). However, bearing in mind that the authors of these studies [21,55] assessed the average energy of ions that have passed to the solution from the anodic microdischarge zone as 100 eV, it can be assumed that the yield per 100 eV coincides with the yields expressed as the number of moles per Faraday of electricity. This allows one to compare certain values found for the glow discharge and anodic microdischarges (Table 9).

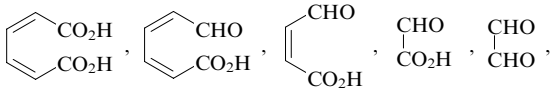
Table 9. Yields of products (mol F^{-1}) under the action of a glow discharge [38] and anodic microdischarges [21,55] on an aqueous ethanolic solution.

$[C_2H_5OH]$ /mol litre^{-1}	CH_3CHO			Butane-2,3-diol	
	glow discharge in O_2	glow discharge in Ar	anodic microdischarge	glow discharge in Ar	anodic microdischarges
0.01	0.18	0.25	–	0.05	–
0.1	2.39	1.83	0.024	0.90	0.0007
0.3	6.47	4.67	0.043	1.14	0.0015
0.9	6.44	4.56	–	1.20	–
1.0	–	–	0.14	–	0.078

The difference between the yields obviously exceeds the possible errors and may point to a difference in the mechanisms of processes in these PSS.

b. Oxidation of aromatic compounds under pulsed discharges

Since the early 1990s, in line with the solution of environmental problems, keen attention has been paid to the oxidation of aromatic compounds in aqueous solutions under the action of either pulsed discharges in liquids or pulsed discharges between a metal electrode located in the gas phase and the solution surface.[55–69] These studies preferentially dealt with phenol and its derivatives. In the phenol oxidation generated by pulsed discharges, pyrocatechol, hydroquinone, *p*-benzoquinone and (in small amounts) resorcinol were detected as the primary products.[60,68] Figure 5 shows the kinetics of decomposition of phenol and accumulation of its primary destruction products. Presumably, the first stage of this process is the hydroxyl radical reaction with a phenol molecule, which results in either the addition of HO$^{\bullet}$ to the benzene ring to afford a dihydroxycyclohexadienyl radical or the elimination of a hydrogen atom from the OH group to form a phenoxyl radical. The radical reactions produced the intermediates listed above. Subsequent stages involved the benzene ring opening to form acyclic products



and also oxalic and formic acids, acetaldehyde and formaldehyde. Figure 6 illustrates the kinetics of accumulation of formic acid in aqueous phenol subjected to a corona discharge.[60]

The oxidation of phenol in aqueous solutions under anodic microdischarges was described.[22,70] For relatively low initial phenol concentrations ($\sim 10^{-5}$–10^{-2} mol litre^{-1}), its concentration was found to decrease in time according to the exponential law; however, for high initial concentrations, two characteristic kinetic regions were observed, namely, the initial fast and the subsequent slow regions. Presumably, the deceleration of the oxidative destruction of phenol observed in its concentrated solutions was associated with the accumulation of stable intermediates and their competition with phenol molecules for HO$^{\bullet}$ radicals.

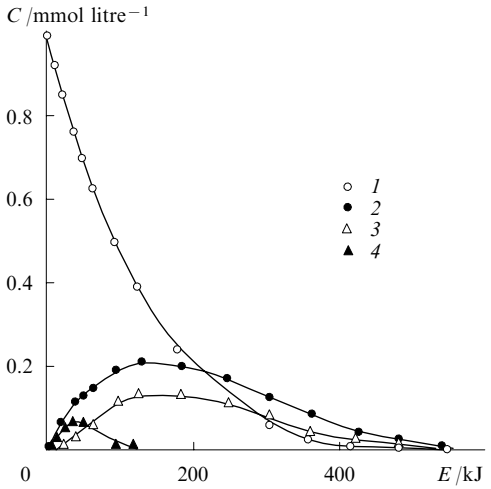


Figure 5. Kinetics of oxidation of phenol and accumulation of its primary destruction products: (*1*) phenol, (*2*) pyrocatechol, (*3*) hydroquinone, (*4*) *p*-benzoquinone.

c. Oxidation of organic dyes in aqueous solutions

The corona-discharge generated oxidation of Methylene Blue and Malachite Green dyes in aqueous solutions was studied [71]

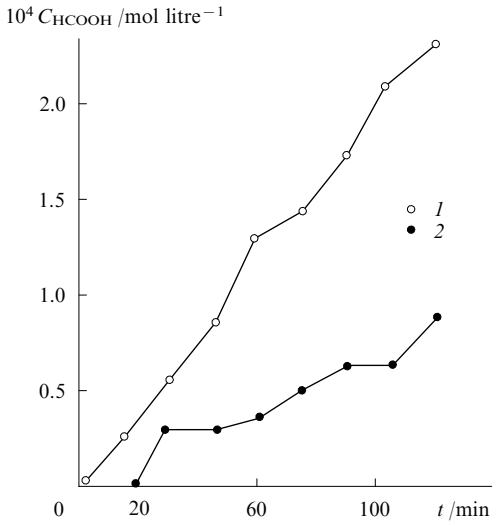


Figure 6. Kinetics of formic acid accumulation under the action of a pulsed corona discharge on an aqueous phenol solution: (*1*) in argon, (*2*) in air.[60]

(the solution volume was 100 ml, the starting concentrations of dyes was 6 mg litre^{-1}, the discharge current was varied from 40 to 150 μA). The kinetics of this process was monitored by following variation of the light absorption by the dissolved dye. The results strongly depended on stirring and the distance between the electrode and the solution surface. Chloride ions inhibited this process. Presumably, ozone, oxygen atoms, HO$^{\bullet}$ radicals and hydroxyl ions were the active species that initiated the dye oxidation. After the treatment, the solution ceased to absorb light at 200–900 nm.

The oxidation of an aqueous solution of Monochlorotriazine Blue (or Bright Blue) dye (MCTB) under glow or gliding arc discharges was considered.[72,73] In all experiments, the dye was decolourised (Fig. 7). However, the initial period of this process could be different for different discharge currents and types. Thus when the times of MCTB exposure did not exceed 2–3 min, the absorption could uniformly decrease over the whole visible spectrum range; however, the process could lead to a decrease in the absorption in the vicinity of the maximum ($\sim$600 nm) and its simultaneous increase in the vicinity of the

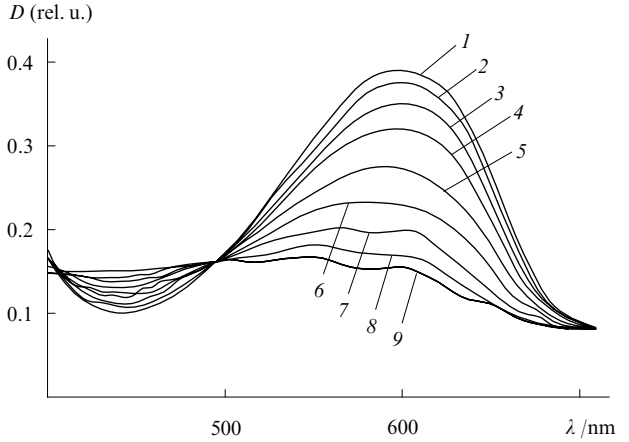


Figure 7. Changes in the absorption spectrum of a solution of Chlorotriazine Blue under a gliding arc discharge.
Exposure time (min): (*1*) 0, (*2*) 2, (*3*) 4, (*4*) 6, (*5*) 8, (*6*) 10, (*7*) 12.5, (*8*) 15, (*9*) 17.5.

absorption minimum ($\sim$450 nm). For long-term exposure, the absorption at 450 nm passed through a maximum and the absorption in the near UV range increased. The changes in the absorption spectrum of the dye could be observed for several hours after the cessation of the plasma treatment.

Based on the results of specrophotometric measurements, kinetic curves that reflect the changes in the dye concentration were plotted. In doing so, it was assumed that oxidative destruction products of a dye do not absorb in the long-wave region. Figure 8 shows the examples of kinetic curves.

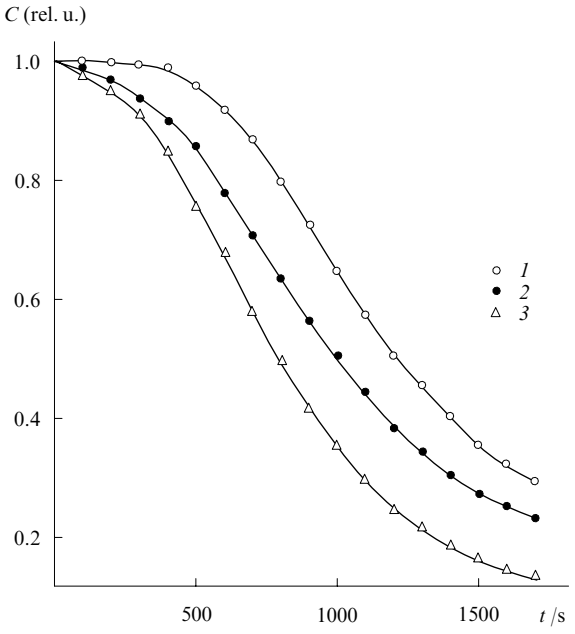


Figure 8. Kinetics of destruction of Monochlorotriazine Blue under a glow discharge with the plasma zone of different length (mm): (*1*) 1.34, (*2*) 2.3, (*3*) 3.8.

Experimental kinetic curves were interpreted within the framework of a simple model that assumes the plasma-initiated formation of an oxidant and its one-stage reaction with the dye, which is of the first order with respect to the oxidant. The rate of oxidant formation (ω_o) is constant within the framework of this model. The accumulation of oxidant after switching on the discharge is determined by ω_o and the oxidant lifetime (τ_o). The model gives the following expression for the time dependence of the relative dye concentration (C/C_0):

$$\ln\frac{C}{C_0} = -\left(\frac{k\omega_o\tau_o}{2}\right)t^2 - (k\omega_o\tau_o^2)(e^{-t/\tau_o} - 1),$$

where k is the effective rate constant for oxidation.

Figure 8 shows the dependence of the dye oxidation rate on the distance between the anode and the solution surface. An increase in the discharge current results in the substantial acceleration of the dye destruction (Fig. 9). Extrapolation to the zero inter-electrode distance gives the reaction rate for the solution activation by exclusively the ions accelerated in the region of the near-surface potential drop and injected into the liquid phase. The increase in the reaction rate with the increase in the plasma column height points to the possibility of initiation of the reaction by neutral active species generated in the gas phase.

The effect of the pre-treatment of a MCTB solution with a corona discharge on the rate of the MCTB oxidation under a stationary glow discharge was studied.[29] For the treatment

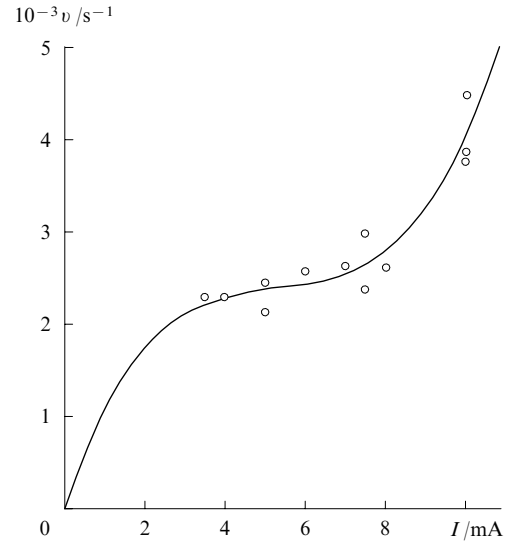


Figure 9. Initial destruction rate of Monochlorotriazine Blue during the plasma treatment *vs.* discharge current (the rate was assessed from the changes in the optical density of solution).

time of no longer than 30 min, the decolouration of the solution under the direct action of a corona discharge with a current of 50 – 100 μA was hardly visible. At the same time, the subsequent oxidation of the dye under the action of a glow discharge sharply accelerated.

The oxidation of Methylene Blue in aqueous solutions under the action of glow and diaphragm discharges was considered[74, 75] (the current was varied in a range of 20 – 50 mA). The kinetics of dye destruction was studied using a spectrophotometric technique in wavelength ranges of 220 – 350 and 450 – 750 nm (λ_{max} = 667 nm) with periodic sampling of the solution.

Discharges of both types favoured a decrease in the optical density of solutions in the visible spectrum of the dye. In an acidic medium (pH < 4), the increase in the discharge current led to the acceleration of dye destruction. It should be noted that for all other factors equal, the decolouration was faster at the diaphragm discharge. The absorption spectra in the region of 450 – 750 nm remained virtually unchanged, being identical for both discharge types. At the same time, the changes in the UV spectrum substantially depended on the discharge type. The increase in the optical density of solutions with the increase in the time of their exposure to plasma was one order of magnitude greater for the glow discharge (for equal exposure times and similar discharge currents and pH values). This fact can be interpreted as a result of the deeper oxidative destruction of the dye under the action of a diaphragm discharge. Presumably, these results point to the difference in the mechanisms of processes initiated by glow and diaphragm discharges. This was assumed to be due to the effect of a shock wave that appears during the burning of a diaphragm discharge.

In the same publications, the post-effect, which was observed in solutions treated with a discharge was discussed. The studies were carried out by several methods.

1. Dye solutions (pH 3) were exposed to the plasma of the glow and diaphragm discharges at a current of 50 mA for 2, 5 and 10 min, then samples were taken and the time variations of the absorption spectra in the absence of plasma treatment were studied.

2. Electrolyte solutions ($H_2O + H_2SO_4 + Na_2SO_4$) with pH 3 were exposed to discharges of both types for 2, 5 and 10 min; immediately a dye was added up to a concentration of

0.01 g litre^{-1}. Then, solution samples were taken and their absorption spectra were analysed in certain time intervals.

3. Experiments were carried out as described above (point 2), but the dye was added in 20 min rather than immediately.

The deviations in the effects of glow and diaphragm discharges also showed up in the post-effect characteristics. Under the same conditions, the diaphragm discharge produced a stronger effect (Fig. 10). Upon the cessation of the discharge, the dye concentration decreased to the same level for both the direct plasma treatment of dye solutions and when the dye was added to the electrolyte pre-activated by a discharge. At the same time, the kinetics of the post-effect strongly depended on the experimental conditions, *e.g.*, on the illumination (Fig. 11).

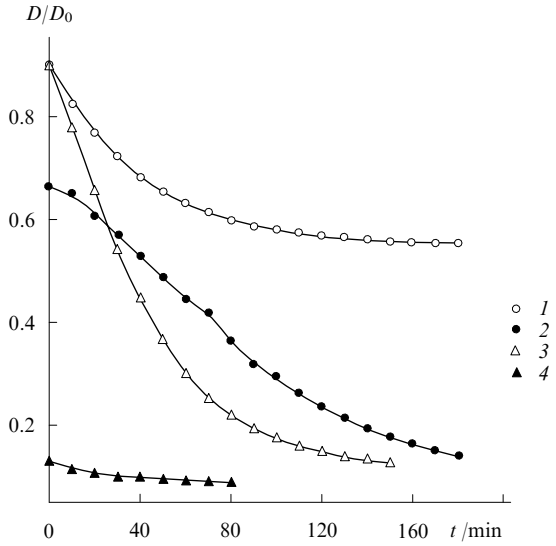


Figure 10. Changes in the optical density of a Methylene Blue solution upon its exposure to plasma (discharge current 50 mA, pH ~ 3, λ_{max} = 667 nm): (*1*) glow discharge, exposure time 5 min; (*2*, *3*, *4*) diaphragm discharge (exposure times 2, 5 and 10 min, respectively).

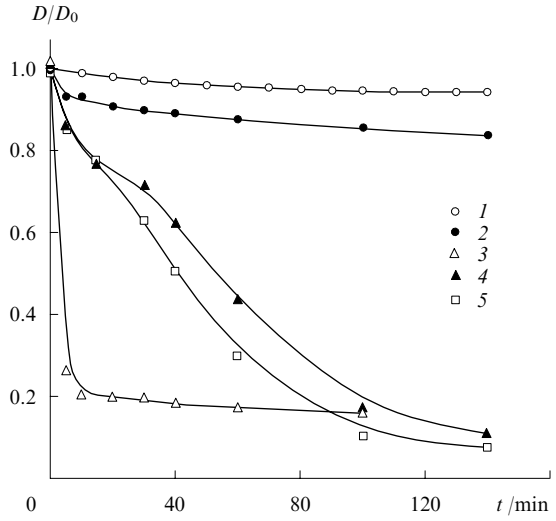


Figure 11. Changes in the optical density of a plasma-pre-activated Methylene Blue solution.
(*1*) Glow discharge: exposure time 10 min, the solution was kept in the dark; (*2–5*) diaphragm discharge: exposure time 10 min (*2*) in the dark and (*3*) in the light; exposure time 5 min (*4*) in the dark and (*5*) in the light.

To explain the results obtained, it was assumed that, in principle, the exposure of solutions to gas discharges can give rise to three different effects, namely, solution activation, solute activation and changes in the solution structure. Among these effects, only the solution activation is sufficiently well studied. Insofar as the differences between the glow and diaphragm discharges were observed both at their direct action on dye solutions and as the post-effect in preliminary treated dye solutions and also as the changes in the destruction rate of a dye added to electrolyte solutions (pre-treated with a discharge in the absence of the dye), the role of direct activation of the solute can hardly be great. At the same time, the post-effect could not be caused by short-lived primary active species; and, moreover, the addition of hydrogen peroxide to a dye solution, which was not pre-treated with a discharge, did not lead to results resembling the post effect. Thus, the reason for the long-term and strong post-effect should be sought in the effect of the discharge on the solution structure, which can cause changes in both thermodynamic and kinetic characteristics of processes that occur in solutions. This effect can be stronger in the presence of a shock wave at the diaphragm discharge.

d. Syntheses of organic compounds initiated by a gas discharge in electrolyte solutions

Harada and co-workers [76, 77] studied the asparagine formation under the action of a glow discharge on a solution containing a mixture of amino acids (glycine, alanine and β-alanine) with amides of simple carboxylic acids.

Denaro and Hough [78] studied the acrylamide polymerisation initiated by a glow discharge between the air-located metal anode and an aqueous solution of the monomer. They have found the dependences of the polymer yield and its average molecular mass on the quantity of electricity passed, the acrylamide concentration and the air pressure. The results obtained were explained within the framework of a simple kinetic model. Two reaction zones were singled out. The first zone represented a thin near-surface solution layer in the vicinity of the cathodic spot. No polymerisation was observed in this zone. The concentration of radicals in this zone was very high; hence, their recombination prevailed. Only ~0.2% of radicals reached the second zone with a volume of ~0.4 cm^3. Here, the radicals initiated the chain polymerisation reaction. The polymer yield increased virtually linearly with the increase in both the quantity of passed electricity and the acrylamide concentration. The average molecular mass also increased linearly with the increase in the monomer concentration. Under the conditions of the experiment described, the polymer yield reached 15 mol F^{-1}. With the increase in the air pressure, these characteristics decreased. Moreover, the efficiency of this process also decreased in the alkaline medium.

V. Potentials and prospects of plasma initiation of industrial processes in aqueous solutions

The surface modification of polymeric materials including fabrics with natural and synthetic fibres (pre-treatment of fabrics before printing, dying, *etc.*), bleaching (especially of linen), delignification of wood, *etc.* may be assigned to the heterogeneous processes presumably initiated by the plasma–solution treatment. At present, this field remains virtually unexplored.

1. Plasma modification of starch glue. Treatment of microcrystalline cellulose

The modification of starch by different reagents is one of the methods used in practice for the preparation of starch and its products with desired properties. The treatment of starch with oxidants, for example, sodium or potassium hypochlorites, is most popular. Hydrogen peroxide, potassium permanganate

in alkaline media, chloramine T, *etc.* are also used. The diverse goals of starch modification, the long time required when traditional methods are used and the environmental problems associated with the use of such reagents as hypochlorites send the scientists in search for alternative methods of modification. The effect of the glow-discharge plasma treatment on the properties of starch glue was studied.[79,80] The glue viscosity was considered as the criterion of its modification degree. The viscosity was observed to increase in the initial period of treatment. The decrease in the viscosity at long-term treatment pointed to the predomination of destruction processes. Note that it takes a short time to reach the maximum viscosity even for discharges with quite moderate power densities.

The use of atmospheric-pressure plasma in processing of cellulose-containing materials attracts attention because cellulose is one of the basic raw materials used in the pharmaceutic, textile and food industries. The surface modification of cellulose by the gas-discharge activation can change its reactivity.

The effect of gas-discharge activation on the electrokinetic properties of aqueous suspensions of cellulose powder (electrophoresis mobility of cellulose particles) was considered.[81] Glow and diaphragm discharges served as the sources of activation. A 0.04% solution of cellulose powder with colloid particles <63 μm in diameter was studied. The required solution conductivity was achieved by adding sodium chloride (10^{-3} mol litre^{-1}). The acidity of the dispersed medium was controlled by the addition of sodium hydroxide or hydrochloric acid. The studies of the electrophoretic mobility of processed cellulose have shown that the isoelectric point is at pH 2.5 and the maximum electrophoretic mobility is reached at pH 6.5. The exposure (20 min) of the dispersed system studied to the discharge led to the increase in the electrophoretic mobility of cellulose particles as compared with the reference untreated solution; moreover, the greatest effect was observed for the glow discharge. The latter effect can be associated with the fact that a diaphragm discharge not only generates reactive species but also gives rise to a shock wave in the solution.

2. Destruction of aqueous emulsions of hydrocarbons in anodic microdischarges

Under the action of an anodic microdischarge (aluminium cathode) on a pentadecane emulsion in a carbonate electrolyte, the alkane is destroyed to form hydrogen, carbon monoxide, gaseous hydrocarbons and an insoluble product, namely, a polycondensate that gives rise to the formation of spherical hollows filled with gas.[82–85]

It was assumed that the primary process is the reaction between pentadecane and a hydroxyl radical, which consists of the elimination of a hydrogen atom from the alkane. A secondary aliphatic radical formed can either dimerise to afford a branched product or add an oxygen molecule. In turn, the peroxide radical gives rise to various secondary products, namely, alcohols, ketones, acids, hydroperoxides. The appearance of spherical particles points to the formation of a three-dimensional network; hence, dimeric products are subjected to the secondary attack of HO$^{\bullet}$ radicals and decomposition products of hydroperoxides or react with fragment radicals formed in gas–vapour bubbles (GVB).

The energy yields of gaseous hydrocarbons C_1-C_5 and CO were independent of the emulsion concentration in the liquid phase. The overall curves of accumulation of gaseous products were linear for degrees of pentadecane conversion not exceeding 50% (at higher degrees of conversion, the curves tended to a certain limit). The partial curves of accumulation of individual gases with the exception of hydrogen were linear. The sum of energy yields of gaseous products increased non-linearly with the increase in the pentadecane concentration. The destruction of pentadecane to form light hydrocarbons almost totally proceeded within gas–vapour bubbles. Hydrogen molecules were largely formed in the pentadecane layer on the GVB surface upon the reaction of the hydrogen atoms formed in GVB with pentadecane molecules. Carbon monoxide was also formed in GVB but upon the oxidation processes.

The microdischarge treatment of an emulsion containing 0.0012 mol litre^{-1} of pentadecane and 0.005 mol litre^{-1} of styrene resulted in the destruction of both pentadecane and styrene in energy yields of 0.16 and 0.50 molecules, respectively, per 100 eV of consumed energy, which was close to their yields in emulsions containing only individual components.[86]

3. Plasma treatment of cellulose-containing and other phytogenic materials in aqueous media. Refining of textile materials

In addition to the search for new kinds and sources of raw materials, the development of fundamentally new methods for processing of traditional raw materials is of great importance. The processing of wood and resulting cellulose (including microcrystalline cellulose) forms the basis of many industrial processes (in pulp and paper industry, manufacturing of synthetic fibres, *etc.*).

Traditional processing of wood into cellulose, which involves mechanical grinding of wood, removal of lignine, (*e.g.*, by sulfite-alkaline digestion), bleaching, washing and drying, is an energy-consuming process accompanied by the formation of vast amounts of toxic sewage.

Thus, the plasma–solution activation of the listed processes in the stationary (or quasi-stationary) plasma or pulsed-discharge plasma in the liquid phase attracts attention. In these two cases, the chemical activation conditions are different; moreover, pulsed discharges give rise to a shock wave, *i.e.*, lead to the mechanochemical activation.

The studies of the effect of pulsed discharges in aqueous media on raw plant materials date back to the1970s. Thus it was shown [86] that the processing of winter wheat straw in water and weak alkaline solutions leads to the partial destruction of the lignocarbon complex in straw and can form the basis of an industrial process of straw treatment for feeding livestock. It was proposed [87] to use high-voltage pulsed discharges in aqueous media for washing and degreasing wool. It was shown [88] that the electrohydraulic treatment of chlorella improves the digestibility of nitrogen-containing substances, while the similar processing of pine needles [89] makes it possible to produce a vitamin–protein concentrate. The action of pulsed discharges in water on kitchen herbs (parsley, dill) leads to the formation of a protein–lipid complex, a precursor of the vitamin–protein paste.[90] It was found [91] that the electrohydraulic treatment of aqueous solutions of saccharose and glucose results in their hydrolysis, where a part of molecules decompose to afford formaldehyde. The possibility of using pulsed discharges at different stages of the wet treatment processes in industry, including textile production, was studied.[92] A method for production of fibres from stems of fibre crops in which the wetting procedure was combined with high-voltage discharges at a voltage of 30–50 kV has been developed.[93]

Detailed studies of the pulsed-discharge treatment of plant raw materials in aqueous media were carried out later.[94,95] Wheat straw (coarse chopped, 3–10 mm) was subjected to pulsed discharges in water and the aqueous solutions of NH_4OH (0.5%–5%) and hydrogen peroxide (1%–5%). A stainless-steel reactor served as the cathode, a cylindrical anode was placed at the reactor axis above the solution surface. A power source allowed application of voltage pulses of 20–35 kV at a frequency of 0.1–0.5 Hz, period of 4–5 μs and energy of 120–2500 J. The treatment involved series of 100–1000 pulses. Both liquid and solid phases of the system formed upon the action of pulses were analysed. Table 10

Table 10. Liquid phase characteristics (in % of the original straw mass) after 100 discharge pulses as a function of single-discharge energy.[94]

Determined characteristics	Discharge energy /J				
	120	240	540	960	2500
Extractive substances	0.04	0.09	0.55	0.13	0.58
Lignine	0.32	0.27	0.25	0.42	0.6
Polysaccharides	0.05	0.06	0.07	0.08	0.04
Colloidal suspension	1.1	1.2	1.0	1.5	1.5
Ash content	0.33	0.51	0.56	0.69	1.0

shows the results of the analysis of the liquid phase after 100 pulses with different energies.

Under the electrohydraulic impact, wheat straw is effectively chopped and its lignine–carbon complex is destroyed. The solid residue is freed from nitrogen-containing (proteins and their products) and silicon-containing compounds that enter into the ash composition. The short-term destruction of the lignine–carbon complex is the characteristic feature of the electrohydraulic treatment of plant biomass. The deeper destruction of the lignine–carbon complex was observed in the processing of wheat straw in NH_4OH and H_2O_2 solutions; although, due to the high conductivity of these solutions, a part of energy was consumed in the pre-breakdown stage, which affected the effectiveness of the electrohydraulic impact.

Similar processes occurred in alkaline aqueous suspensions of hydrolytic lignine, which were subjected to high-voltage pulsed discharges.[95] Lignine was dispersed and freed from mineral and organic low-molecule substances. However, gummy and lignohumic compounds were not removed. The gummy substances were washed out in alkalis, which was considerably accelerated under the simultaneous treatment with electric pulses.

All aforementioned studies devoted to the use of pulsed discharges failed to separate the contributions of chemical process and mechanochemical activation.

The effect of the solution activation in a glow discharge on the surface properties of cellulose-containing materials placed in solutions and also on the extraction of lignine was studied.[29,96] Linen and roving fabrics were studied as well as wood in the form of sawdust. The process was carried out in aqueous NaOH at constant stirring, either without the gas flow or with oxygen bubbling through the solution. A 'positive' stationary glow discharge was used. It was found that the plasma–solution treatment allows one to increase the capillarity of fabrics; moreover, the effect strongly depended on the solution pH and might not correlate with the lignine destruction.

To check the selectivity of the effect of an activated solution on the cellulose-containing materials, the products obtained in the treatment of delignified cellulose and wood-extracted lignine, which have passed to solution, were analysed separately. The effect was followed by the analysis of absorption spectra of treated solution samples. Figure 12 shows the results obtained in an alkaline solution after the treatment of cellulose (with and without plasma activation) and lignine. According to these data, a plasma-activated aqueous solution that contains no specially added oxidants exerts a selective effect on the cellulose-containing materials.

The presence of such selectivity allows one to assume the possibility of using the mentioned method in the bleaching of fabrics. The samples of linen fabric were treated in the plasma-activated solution in the absence of specially added oxidants. The absorption spectra of the solution and the scattering spectra of the fabrics were studied simultaneously. The results obtained confirmed that the effect of fabric bleaching is present

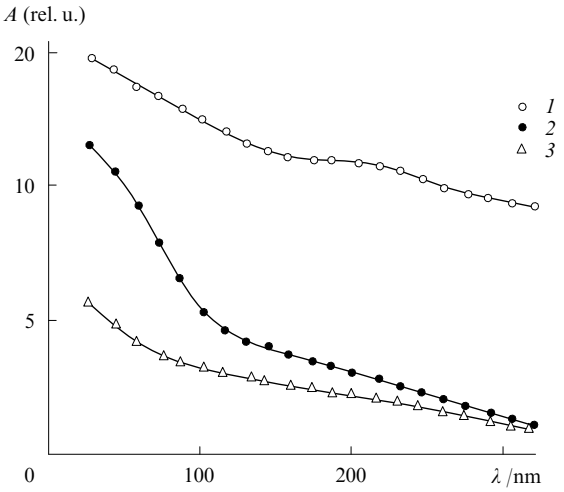


Figure 12. Absorption spectra of solutions of (*1*) lignine and (*2*) cellulose upon treatment in a glow discharge (NaOH solution with concentration 1 g litre^{-1}, discharge current 20 mA, exposure time 20 min) and (*3*) spectrum of a solution of cellulose unexposed to plasma.

and the products accumulated in solution substantially affect this process.

The use of a volume discharge described quite recently in the treatment of cellulose-containing materials in the plasma–solution system was discussed.[97] Presumably, to achieve the greatest effect in the modification of polymeric materials, it is necessary to develop a PSS in which the reactions in the activated solution would occur simultaneously with the direct effect of plasma on the material modified. The discharge was ignited in a tube of silicon rubber that connected two stainless-steel vessels, which served as the electrodes; the circulation of solution was performed using a peristaltic pump. Linen roving of four-fold milling and purified cellulose were studied. The average degree of polymerisation, the lignine content and the moisture absorption were measured for the case of linen roving. In the case of cellulose, the measured characteristics included the degree of polymerisation and the contents of α-cellulose and the aldehyde and carboxyl groups. The treatment time was 10 min.

The treatment of linen roving in a PSS with a discharge in the electrolyte volume (NaOH) resulted in a greater decrease in the lignine content as compared with the conventional thermal

Table 11. Properties of linen roving treated in a plasma–solution system (volume discharge).[97]

Sample	C_{NaOH} /g litre^{-1}	Lignine content [a] (%)		Degree of polymerisation	Moisture absorption (%)
		ASL	AIL		
Original roving (4-fold milling)		1.5	10.5	4750	1010
Samples after treatment					
boiling [b]	50	0.4	9.3	3200	980
discharge [c]	50	0.21	5.2	2986	1030
boiling [b]	100	0.5	8.8	5500	1250
discharge [c]	100	0.2	4.6	1450	1142
boiling [b]	150	0.42	9.2	4500	1210
discharge [c]	150	0.19	4.6	2785	1205

[a] ASL and AIL are acid-soluble and acid-insoluble lignine, respectively; [b] at 98 °C for 1 h; [c] in solution for 10 min.

Table 12. The effect of cellulose treatment in a volume discharge on its physicochemical properties.[97]

Treatment conditions			Degree of polymerisation	Content of α-cellulose (%)	$10^5\,\delta$ (see [a]) (%)
C_{NaOH} /g litre^{-1}	time /min	tube diameter /mm			
Original sample			1400	91.4	5.3
50	20	10	825	93.24	3.39
50	20	8	905	91.3	3.51
50	15	8	900	90.7	3.76
10	30	10	940	89.4	2.9
10	15	10	960	88.1	3.3
10	15	8	892	91.84	2.98
5	20	8	959	88.67	3.47
See [b]	20	8	981	88.77	2.98

[a] δ is the content of aldehyde groups; [b] in this case, the electrolyte was 0.1 M Na_2SO_4.

treatment in alkali with a longer exposure time. The plasma – solution treatment in the volume discharge sharply reduced the degree of polymerisation; however, the moisture absorption changed insignificantly (Table 11). Table 12 shows the data obtained in the studies of cellulose.

4. The use of plasma – solution systems in cleaning and sterilisation of water, aqueous solutions and articles

The use of plasma discharges in aqueous media for their sterilisation and also for the sterilisation of articles was extensively studied since the beginning of the 1970s.[98–106]

High-voltage electropulsed discharges can be considered as an environmentally clean source of UV radiation the short-wave spectrum of which is not 'cut off' by glass walls as in the case of UV lamps. Under the action of reactive species formed in water, decomposition of amino acids and proteins, depolymerisation of nucleic acids and destruction of other biologically active substances take place. Moreover, a pulsed discharge generates intense acoustic waves capable of tearing apart bacterial cells thus destroying them. The disinfecting effect persists for a long time after the cessation of the discharge treatment (days, weeks and longer) due to the effect of the microorganism decomposition products obtained in the active phase of the process. According to the data of Ref. 106, the pronounced antibacterial effect was observed at a discharge energy of $(0.6-0.8)\times10^2$ J. In the same study, quantitative estimates of energy consumed in the water disinfection were obtained. The calculated relationships were derived under the assumption that the main effect is associated with the shock wave impact and that the destruction of simplest unicellular microorganisms requires an acceleration of 100 – 1000 g. The pressure in the compression wave front was assessed by the semi-empiric relationship

$$P = 0.6\times10^{-5}\,E_0^{0.6}\tau^{-0.8}r^{-1},$$

where P is the pressure (mPa), E_0 is the discharge energy (J), τ is the time of energy generation (s), r is the distance from the discharge centre to the measurement point (m).

If ρ_0 and a_0 are the density of the liquid and the sound velocity in it, then the liquid acceleration in the wave is

$$W = \frac{2P}{\rho_0 a_0 \tau}.$$

Hence, for the relative acceleration K_p, we obtain the following expression:

$$K_p = \frac{2P}{g\rho_0 a_0 \tau} = 0.8\times10^{-5}\,\frac{2E_0^{0.6}}{gr\rho_0 a_0 \tau^{1.8}}.$$

The volume of water cleaned is assessed from the distance at which the acceleration of the liquid in a wave is not lower than a given critical value.

The disinfecting efficiency of an atmospheric-pressure glow discharge that burned over the water surface in a flow-through system was assessed.[107] The concentration of hydrogen peroxide formed under the discharge (the discharge current was 200 mA, the output voltage reached 5 kV) was taken as the criterion of water decontamination efficiency. For a discharge gap of 10 mm and the power of ~90 W, the maximum accumulation of hydrogen peroxide was observed, namely, 3.6 g m^{-3} (1×10^{-4} mol litre^{-1}) at the minimum energy consumed in its formation (~250 kW h kg^{-1}). The fact that the maximum H_2O_2 concentration was achieved under these conditions was attributed to the maximum area of the cathodic spot. The hydrogen peroxide concentration decreased with an increase in the water consumption, whereas the efficiency with respect to H_2O_2 increased. This was explained by the fact that a part of hydrogen peroxide synthesised in the discharge was destroyed by the discharge itself. As a result, at the higher water consumption, the larger amount of H_2O_2 was brought out from the discharge zone without destruction. The overall content of hydrogen peroxide also depended on the electrode erosion products, which often catalyse H_2O_2 decomposition.

Sterilisation of conducting solutions and objects immersed in them under a glow discharge or a low-voltage diaphragm discharge (alternating current) was studied.[33, 108, 109] The inhibiting effect of the atmospheric-pressure glow and diaphragm discharges on asporogenic microorganisms *Escherichia coli* M-17 was discussed. Microbiological studies of strains of the culture tested revealed that totally sterile solutions were obtained in 1 – 20 min depending on the exposure time, the type and intensity of discharge, the nature of the object sterilised and the nature and concentration of the bacterial culture. (Table 13).

Table 13. Results of gas-discharge sterilisation of solutions containing microorganisms *Escherichia coli* M-17 (see [a]).[109]

Composition of the medium [b]	C (see [c])	Treatment time [d] /min		
		DDC	RIF	ECS
Glow discharge				
I	10^4	6	11	16
II	10^4	5	10	15
	10^7	10	16	20
Diaphragm discharge				
II	10^4	1	2.5	3
	10^7	5	10	12

[a] Discharge parameters. Glow discharge: current 50 mA, voltage 1500 V; diaphragm discharge: current 50 mA, voltage 500 V; [b] Composition of the medium: (I) aqueous NaOH solution (1.5 g litre^{-1}) and nitrilotrimethylphosphonic acid; (II) physiological solution of NaCl (2 g litre^{-1}); [c] C is relative concentration of microorganisms (number of colonies in 1 ml of solution); [d] treatment time necessary for a decrease in the density of colonies (DDC), for observation of rare individual formations (RIF), for reaching the effect of complete sterility (ECS).

VI. Conclusion

Plasma – solution systems in which an electrolyte solution plays the role of one or both gas-discharge electrodes represent non-equilibrium systems where the chemical activation predominantly proceeds in a thin near-surface solution layer and is substantially determined by the parameters of the gas discharge and related processes on the plasma – solution interface. The combination of the chemical activity of plasma with the possibility of carrying out selective processes in solutions allows one to use plasma – solution systems in cleaning of water and aqueous solutions from organic and inorganic impurities, sterilisation of solutions and objects immersed in them and also in the modification of surface properties of natural and synthetic polymeric materials.

The physical chemistry and physics of PSS were studied far less comprehensively than the corresponding properties of the classical reduced and atmospheric pressure plasma in contact with solid objects. The most important trends in the physicochemical studies of PSS are associated with the kinetics of generation of reactive species in both the solution surface layer and the adjacent plasma layer and also with the reactions of these species depending on the type of initiating gas discharge and the properties of the solution. It is the processes at the plasma – solution interface that are the governing factor.

References

1. M N Vasil'ev, in *Entsiklopediya Nizkotemperaturnoi Plazmy. Vvodnyi Tom IV* (Encyclopaedia of Low-temperature Plasma. Entrance Volume IV) (Ed. V E Fortov) (Moscow: Nauka, 2000) p. 331
2. A Güntherschulze *Z. Electrochem.* **31** 187 (1925)
3. A Klemenc, H F Hohn *Z. Phys. Chem., Abt. A* **154** 385 (1931)
4. A Klemenc, R Eder *Z. Phys. Chem., Abt. A* **179** 1 (1937)
5. A Klemenc, H Kalisch *Z. Phys. Chem., Abt. A* **182** 1 (1938)
6. A Klemenc, G Heinrich *Z. Phys. Chem., Abt. A* **183** 217 (1938)
7. A Klemenc *Z. Phys. Chem., Abt. A* **183** 297 (1938)
8. R A Davies, A Hickling *J. Chem. Soc.* 3595 (1952)
9. A Hickling, J K Linacre *J. Chem. Soc.* 711 (1954)
10. A R Denaro, A Hickling *Electrochem. Soc.* **105** 265 (1958)
11. A Hickling, G R Newns *J. Chem. Soc.* 5177 (1961)
12. A Hickling, G R Newns *J. Chem. Soc.* 5186 (1961)
13. A Hickling, M D Ingram *Trans. Faraday Soc.* 783 (1964)
14. A Hickling, in *Modern Aspects of Electrochemistry* Vol. 6 (Eds J O M Bockris, B E Conway) (London: Butterworth, 1971) p. 329
15. A Hickling, M D Ingram *J. Electroanal. Chem.* **8** 65 (1964)
16. A R Denaro, A Hickling *J. Electrochem. Soc.* **105** 265 (1958)
17. V V Bakovets, O V Polyakov, I P Dolgovesova, in *Plazmenno-elektroliticheskaya Anodnaya Obrabotka Metallov* (Plasma-electrolytic Anodic Metal Working) (Novosibirsk: Nauka, 1991) p. 168
18. O V Polyakov, V V Bakovets *Khim. Vys. Energ.* **17** 291 (1983) [a]
19. E G Vol'f, L T Bugaenko, G V Kovalev, A M Sizikov, E P Kalyazin *Khim. Vys. Energ.* **22** 377 (1988) [a]
20. L T Bugaenko, E G Vol'f, E P Kalyazin, G V Kovalev, A M Sizikov, in *Plazmokhimiya-90* (Plasma Chemistry-90) Pt. 1 (Moscow: Department of Scientific and Technical Information of Institute of Petrochemical Synthesis, Academy of Sciences of the SSSR, 1990) p. 8
21. L T Bugaenko, E G Vol'f, E P Kalyazin, G V Kovalev, A M Sizikov *Khim. Vys. Energ.* **29** 456 (1995) [a]
22. O V Polyakov, A M Badalyan, L F Bakhturova *Khim. Interes. Ustoich. Razv.* **8** 855 (2000) [b]
23. A I Maximov, L A Kuzmicheva, A Y Nikiforov, J V Titova *Plasma Chem. Plasma Proc.* **26** 205 (2006)
24. S Braun *Elementarnye Protsessy v Plazme Gazovogo Razryada* (Elementary Processes in Plasma of Gas Discharge) (Moscow: Gosatomizdat, 1961)
25. A M Kutepov, A G Zakharov, A I Maksimov *Dokl. Akad. Nauk* **357** 782 (1997) [c]
26. A V Khlyustova, A I Maksimov *Elektron. Obrab. Mater.* **217** 35 (2002)
27. A V Khlyustova, A I Maksimov *Elektron. Obrab. Mater.* **227** 79 (2004)
28. A V Khlyustova, A I Maksimov, V A Titov *Khim. Vys. Energ.* **38** 227 (2004) [a]
29. Yu V Titova, Candidate Thesis in Chemical Sciences, Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 1999
30. *Tablitsy Fizicheskikh Velichin* (The Tables of Physical Values) (Ed. I K Kikoin) (Moscow: Atomizdat, 1976)
31. A I Maksimov, Yu V Titova, L A Kuz'micheva, in *Gorenie i Plazmokhimiya (Sb. tr. III Mezhdunarodnogo Simpoziuma), Almaty, 2005* [Combustion and Plasma Chemistry (Proceedings of the IIIrd International Symposium), Almaty, 2005] p. 347
32. A K Pikaev, S A Kabakchi, I E Makarov *Vysokotemperaturnyi Radioliz Vody i Vodnykh Rastvorov* (High-temperature Radiolysis of Water and Aqueous Solutions) (Moscow: Energoatomizdat, 1988)
33. I K Stroikova, Candidate Thesis in Chemical Sciences, Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 2001
34. I K Stroikova, A I Maksimov *Elektron. Obrab. Mater.* **219** 52 (2003)
35. H A Dewhurst, J F Flagg, P K Watson *J. Electrochem. Soc.* **106** 366 (1959)
36. S K Sengupta, O P Singh *J. Electroanal. Chem.* **369** 113 (1994)
37. G A Mazzocchi, G Bontempelli, F Magno *J. Electroanal. Chem.* **42** 3698 (1973)
38. M A Almubarak, A Wood *J. Electrochem. Soc.* **124** 1356 (1977)
39. L A Kuz'micheva, Yu V Titova, A I Maksimov *Elektron. Obrab. Mater.* **228** 57 (2004)
40. A R Denaro, A Mitchell, M R Richardson *Electrochim. Acta* **16** 755 (1971)
41. A R Denaro, P A Owens *Electrochim. Acta* **13** 157 (1968)
42. L A Kuz'micheva, A I Maksimov, Yu V Titova *Elektron. Obrab. Mater.* **233** 41 (2005)
43. J L Brisset, J Lelievr, A Doubla, J Amouroux *Rev. Phys. Appl.* **25** 535 (1990)
44. M Chabchoub, J-L Brisset, A Czernichowski, in *Proceedings of 12th International Symposium on Plasma Chemistry, Minneapolis, 1995* Vol. 2, p. 801
45. A V Khlyustova, Candidate Thesis in Chemical Sciences, Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 2004
46. A I Maksimov, A V Khlyustova, S V Troshenkova *Elektron. Obrab. Mater.* **230** 31 (2004)
47. I K Stroikova, A I Maksimov, A V Grechin, in *Sb. Materialov 3 Mezhdunarodnogo Simpoziuma po Teoreticheskoi i Prikladnoi Plazmokhimii, Ples, 2002* (Proceedings of the 3rd International Symposium on Theoretical and Applied Plasma Chemistry, Ples, 2002) Vol. 2, p. 345
48. A R Denaro, K O Hough *Electrochim. Acta* **17** 549 (1972)
49. A G Zakharov, J V Titova, A I Maximov, in *Problems of Solvation and Complex Formation in Solutions. (Proceedings of the 7th International Conference)*. Ivanovo 1998. P. 420
50. A M Kutepov, A G Zakharov, A I Maksimov, in *Vestn. Khar'kovsk. Un-ta* **27** 1 (1999)
51. Yu V Titova, A I Maksimov *Elektron. Obrab. Mater.* **192** 87 (1998)
52. V I Ksenzenko, D S Stasinevich *Khimiya i Tekhnologiya Broma, Ioda i ikh Soedinenii* (The Chemistry and Technology of Bromine, Iodine and their Compounds) (Moscow: Khimiya, 1979)
53. L A Kuz'micheva, Yu V Titova, A I Maksimov, in *Sb. Materialov 4 Mezhdunarodnogo Simpoziuma po Teoreticheskoi i Prikladnoi Plazmokhimii, Ivanovo, 2005* (Proceedings of the 4th International Symposium on the Theoretical and Applied Plasma Chemistry, Ivanovo, 2005) Vol. 2, p. 121

54. L A Kuz'micheva, Yu V Titova, A I Maksimov, in *Sb. Materialov 4 Mezhdunarodnogo Simpoziuma po Teoreticheskoi i Prikladnoi Plazmokhimii, Ivanovo, 2005* (Proceedings of the 4th International Symposium on the Theoretical and Applied Plasma Chemistry, Ivanovo, 2005) Vol. 2, p. 125
55. L T Bugaenko, E G Vol'f, G V Kovalev, A M Sizikov *Khim. Vys. Energ*. **36** 453 (2002) [a]
56. A K Sharma, B R Locke, P Arce, W C Finney *Hazard. Waste Hazard. Mater*. **10** 209 (1993)
57. A A Joshi, B R Locke, P Arce, W C Finney *J. Hazard. Mater*. **41** 3 (1995)
58. P Sunka, V Babicky, M Člupek, P Lukes, M Simek, J Schmidt, M Černák *Plasma Sourc. Sci. Technol*. **8** 258 (1999)
59. Yu B Bark, E M Barkhudarov, Yu N Kozlov, I A Kossyl, V P Silakov, M I Taktakishvili, S M Temchin *J. Phys. D: Appl. Phys*. **33** 859 (2000)
60. W F L M Hoeben, E M van Veldhuizen, W R Rutgers, C A M G Cramers, G M W Kroesen *Plasma Sourc. Sci. Technol*. **9** 361 (2000)
61. A M Anpilov, E M Barkhudarov, Yu B Bark *J. Phys. D: Appl. Phys*. **33** 993 (2000)
62. W F L M Hoeben, E M van Veldhuizen, W R Rutgers, C A M G Cramers, G M W Kroesen *J. Phys. D: Appl. Phys*. **32** 133 (1999)
63. B Sun, M Sato, J S Clements *J. Electrostat*. **39** 189 (1997)
64. D Hayashi, W F L M Hoeben, G Dooms, E M van Veldhuizen, W R Rutgers, G M W Kroesen *J. Phys. D: Appl. Phys*. **33** 2769 (2000)
65. A T Sugiarto, M Sato *Thin Solid Films* **386** 295 (2001)
66. D Hayashi, W F L M Hoeben, G Dooms, E M van Veldhuizen, W R Rutgers, G M W Kroesen *J. Phys. D: Appl. Phys*. **33** 1484 (2000)
67. P Sunka *Phys. Plasmas* **8** 2587 (2001)
68. P Luceš, Ph.D. Thesis, Institute of Plasma Physics, Academy of Sciences of Czech Republic, Prague, 2001
69. J Goodman, A Hickling, B Schofield *J. Electroanal. Chem*. **48** 319 (1973)
70. A M Badalyan, O V Polyakov, L F Bakhturova *Goren. Plazmokhim*. **1** 187 (2003)
71. S C Goheen, D E Durham, M McCulloch, O William, in *Chemical Oxidation Technology for the Nineties (Proceedings of the Second International Symposium), Nashville, TN, 1992* p. 356
72. A G Zakharov, A I Maksimov, Yu V Titova *Tekstil. Khim*. **13** 20 (1998)
73. J Janca, S Kuzmin, A Maximov, J Titova, A Czernichovski *Plasma Chem. Plasma Proc*. **19** 53 (1999)
74. I N Sergeeva, Yu V Titova, A I Maksimov *Elektron. Obrab. Mater*. **216** 34 (2002)
75. Yu V Titova, I N Sergeeva, A I Maksimov, in *Sb. Materialov 3 Mezhdunarodnogo Simpoziuma po Teoreticheskoi i Prikladnoi Plazmokhimii, Ples, 2002* (Proceedings of the 3rd International Symposium on the Theoretical and Applied Plasma Chemistry, Ples, 2002) Vol. 2, p. 99
76. T Munegumi, A Shimoyama, K Harada *Chem. Lett*. 393 (1997)
77. K Harada, M Takasaki, H Naraoka, S Nomoto *Origin Life* **14** 107 (1984)
78. A R Denaro, K O Hough *Electrochim. Acta* **18** 863 (1973)
79. I N Sergeeva, Yu V Titova, A I Maksimov, in *Aktual'nye Problemy Khimii i Khimicheskoi Tekhnologii (Tez. Dokl. II Mezhdunarodnoi Nauchno-tekhnicheskoi Konferentsii), Ivanovo, 1999* [Topical Problems of the Chemistry and Chemical Technology (Abstracts of Reports of the Second International Scientific and Technical Conference), Ivanovo, 1999] p. 211
80. I N Sergeeva, Yu V Titova, A I Maksimov, in *Tekstil'naya Khimiya-2000 (Tez. Dokl. II Mezhdunarodnoi Konferentsii), Ivanovo, 2000* [Textile Chemistry-2000 (Abstracts of Reports of the Second International Conference), Ivanovo, 2000] p. 114
81. K N Zheleznov, A I Maximov *Mendeleev Commun*. 214 (2005)
82. A M Sizikov, T A Kalinina, I A Glizdinskii, L T Bugaenko *Khim. Vys. Energ*. **35** 219 (2001) [a]
83. T A Kalinina, A M Sizikov, L T Bugaenko *Khim. Vys. Energ*. **35** 393 (2001) [a]
84. T A Kalinina, A M Sizikov, L T Bugaenko, G V Kovalev *Khim. Vys. Energ*. **36** 156 (2002) [a]
85. T A Kalinina, A M Sizikov, L T Bugaenko, G V Kovalev *Khim. Vys. Energ*. **37** 38 (2003) [a]
86. V I Naumenko, N A Zhuravleva, S A Tarchenko, V A Apostoli *Elektron. Obrab. Mater*. **55** 89 (1974)
87. V N Pisarevskii, V V Kovriga, N A Zhuravleva, A P Yarosh *Elektron. Obrab. Mater*. **56** 81 (1974)
88. L D Pidorenko, M A Yatsko, L L Korinetskaya, V V Petrichenko, in *Mekhanizatsiya i Elektrifikatsiya Sel'skogo Khozyaistva, Kiev, 1975* (Mechanisation and Electrification of Agriculture, Kiev, 1975) No. 32, p. 115
89. M A Yatsko, G M Balan *Zhivotnovodstvo* (12) 38 (1973)
90. M A Yatsko, G M Balan, L L Korinetskaya *Elektron. Obrab. Mater*. **64** 62 (1975)
91. M A Yatsko, L L Khonina, L D Pidorenko *Elektron. Obrab. Mater*. **63** 59 (1975)
92. N E Gevorkyan, S A Khachatryan, N G Grigoryan, in *Elektroavtomatika Tekhnologicheskogo Oborudovaniya Tekstil'noi i Legkoi Promyshlennosti (Tr. I Vsesoyuzn. Nauchno-tekhnicheskoi Konferentsii), Erevan, 1973* [Electroautomation of the Equipment in Textile and Light Industry (Proceedings of the First All-Union Scientific and Technical Conference), Erevan, 1973] S. 178
93. USSR P. 362080; *Byull. Izobret*. (2) 64 (1973)
94. V G Gorokhova, L N Petrushenko, A A Shishko, V G Chernova, N V Ivanova, O A Kolomakina, N A Koshilev, V A Babkin, M G Voronkov *Dokl. Akad. Nauk* **343** 62 (1995) [c]
95. N V Ivanova, A A Shishko, V G Gorokhova, N A Koshilev, N V Lebedev, V A Babkin, M G Voronkov *Dokl. Akad. Nauk* **343** 486 (1995) [c]
96. I N Sergeeva, Yu V Titova, A I Maksimov, in *Aktual'nye Problemy Khimii i Khimicheskoi Tekhnologii (Tez. Dokl. II Mezhdunarodnoi Nauchno-tekhnicheskoi Konferentsii), Ivanovo, 1999* [Topical Problems of the Chemistry and Chemical Technology (Abstracts of Reports of the Second International Scientific and Technical Conference), Ivanovo, 1999] p. 210
97. Yu V Titova, M I Voronova, A I Maksimov, in *Sb. Materialov 4 Mezhdunarodnogo Simpoziuma po Teoreticheskoi i Prikladnoi Plazmokhimii, Ivanovo, 2005* (Proceedings of the 4th International Symposium on Theoretical and Applied Plasma Chemistry, Ivanovo, 2005) Vol. 2, p. 414
98. R A Bretosh, L A Rudenko, A F Urusov *Elektron. Obrab. Mater*. **45** 79 (1971)
99. A E Zhuk, E G Zhuk *Elektron. Obrab. Mater*. **64** 60 (1975)
100. L N Zykina, V S Goldaev *Elektron. Obrab. Mater*. **62** 68 (1974)
101. L A Yutkina, O N Mel'nikova, A K Postoev, A Yu Zemlyanoi *Elektron. Obrab. Mater*. **77** 67 (1978)
102. E G Zhuk *Elektron. Obrab. Mater*. **80** 80 (1978)
103. V N Bubentsov, E G Zhuk, Yu V Yakunin *Elektron. Obrab. Mater*. **85** 42 (1983)
104. N D Ryazanov, E N Perevyazkina *Elektron. Obrab. Mater*. **122** 43 (1984)
105. A P Shvedchikov, E V Belousova, A V Polyakova, A Z Ponizovskii, V L Goncharov *Khim. Vys. Energ*. **27** 63 (1993) [a]
106. A G Ryabinin *Elektron. Obrab. Mater*. **176** 77 (1994)
107. A A Ivannikov, V M Lelevkin, A V Tokarev, V A Yudanov *Khim. Vys. Energ*. **37** 148 (2003) [a]
108. Russ. P. 2195961; *Byull. Izobret*. (1) (2003)
109. I K Stroikova, A I Maksimov *Elektron. Obrab. Mater*. **218** 43 (2002)

[a] — *High Energy Chem. (Engl. Transl.)*
[b] — *Chem. Sust. Develop. (Engl. Transl.)*
[c] — *Dokl. Chem. (Engl. Transl.)*