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Mendeleev Commun., 2007, **17**, 294–295

Mendeleev Communications

Transfer of solution components to a plasma zone in chemical reactions initiated by a glow discharge in electrolyte solutions

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DOI: 10.1016/j.mencom.2007.09.016

The role of flows arising in electrolyte solutions under the action of a glow discharge and causing transport processes of solution components to a plasma zone and circulation in a liquid phase was investigated.

One of the simplest plasma–solution systems at atmospheric pressure is a glow discharge, in which one of the electrodes (cathode) is an electrolyte solution.[1] As in case of a classical low pressure glow discharge with metal electrodes, cathode sputtering is typical of this discharge. This is the transfer of the solvent and dissolved compound to a gas phase (nonequilibrium evaporation). The consequence of this process is the arising of streams circulating in the solution volume and compensating the substance outlet to plasma zone (Figure 1).

On the other hand, the excitation of a glow discharge between a metal electrode and an electrolyte initiates redox reactions in solution. Primary reactive particles (H, OH and e_{solv}) are formed in a superficial solution layer under ion bombardment.[1] In spite of a very small thickness of the superficial solution layer (few hundreds of micrometers), they react within this layer.[2,3] Thus, oxidizing processes can take place with the participation of OH radicals in a cathode spot and with the participation of the dimerization product of these radicals, hydrogen peroxide, in the rest solution volume.[2] The ratio between contributions of these channels depends on the rate constants of corresponding reactions.

As found previously,[2,3] an increase of the distance between the solution cathode and the metal anode in air results in the growth of oxidation rate (nearly linear) of an aqueous solution of the monochloroazine dark blue dye. This fact has been explained by the increase of contribution to process of the oxidizing particles, formed in a plasma zone above solution. At the same time, recombination in solution with the participation of hydroxyl radicals is too fast for radicals to reach the solution and to react in a liquid phase.[2] Hence, an additional oxidising effect may be taken by more long-living active forms of oxygen or hydrogen peroxide, formed in the plasma zone. We studied the influence of distance between anode and electrolyte solution surfaces (discharge gap) on hydrogen peroxide formation and on the transfer factor of water molecules to a plasma zone under glow discharge action.

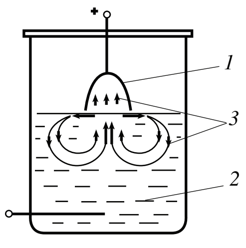

Figure 1 Flows arising in an electrolyte solution under glow discharge action: (*1*) plasma zone, (*2*) electrolyte solution and (*3*) flows.

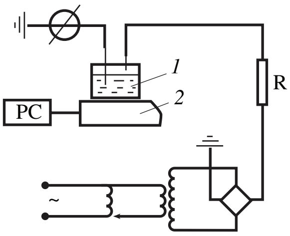

Figure 2 Experimental setup for studying the dependence of the transfer number of solution components to a gas phase on discharge gap: (*1*) glass cell with electrolyte solution, (*2*) electronic scales.

The experimental cell is presented in Figure 1. The anode was an aluminium wire with a diameter of 2 mm. A 0.01 M Na_2SO_4 solution was used as the electrolyte cathode; the solution volume was 50–400 ml. The discharge current was 10 or 20 mA; the plasma treatment time was 30–60 min. The electrolyte solution was not stirred. Hydrogen peroxide in solution after a discharge treatment was determined by iodometric titration with ammonium molybdate.[4] Solution samples were tested after stopping the process and solution mixing. The transfer of solution components to a gas phase was studied by gravimetry. The experimental set is presented in Figure 2. 0.1 M Na_2SO_4 was used as an electrolyte cathode; the solution volume was 60 ml, the discharge current was 10 mA. The transfer number was determined as the ratio of solvent amount passed from solution to gas phase to the positive ion flow.

Solution flows arising in electrolyte solutions were visualised by a Sony Handycam video recorder. Flow rates were obtained at the processing of images on the monitor screen with coordinate scale in real time. In order to obtain images with good resolutions, we used a 0.5 M $BaCl_2$ solution and mixtures of 0.5 M $CaCl_2$ with glycerol.

The dependence of hydrogen peroxide yield on the distance between the metal anode and the solution surface is presented in Figure 3. In spite of our supposition, the decrease of H_2O_2 yield is observed instead of a growth with increasing interelectrode distance. It means that the earlier observed growth of dye destruction rate[2,3] at the increase of discharge gap cannot be explained in terms of dye oxidation by hydrogen peroxide only.

The fact that the H_2O_2 yield decreases with plasma volume excludes a plasma activation effect. Hence, it is necessary to consider the balance of hydrogen peroxide and OH radicals as primary active particles forming H_2O_2. As the bombardment

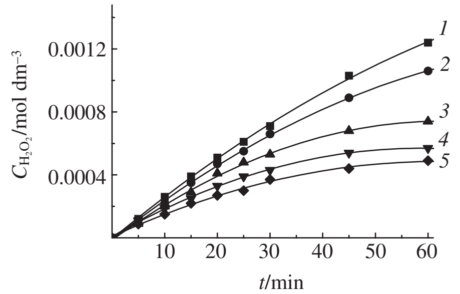

Figure 3 Dependence of the hydrogen peroxide content on discharge gap. (*1*) 0.5, (*2*) 1, (*3*) 2, (*4*) 3 and (*5*) 4 mm (0.01 M Na_2SO_4, 400 ml, 10 mA).

of a solution superficial layer by positive ions from a plasma zone is the only source of generation of OH radicals in a liquid phase, the change of radical yields can be caused by a change of cathode potential drop with varying discharge zone geometry. All measurements of cathode potential drop[1,3] were performed only by varying interelectrode distance. This method supposes plasma properties and cathode potential drop to be independent of plasma zone length. Thus, the need arises to analyse destruction processes of OH radicals and hydrogen peroxide. Rates of these processes can also change with varying discharge gap. The transfer of solution components to gas phase due to ionic bombardment of solution must be taken into account in the balance of these particles. The transfer factor of solvent molecules (water) is extremely high (up to 10^3 mol Faraday^{-1}), and the transfer factor of dissolved substance being approximately proportional to its mole fraction in solution.[2] We suppose this assumption to be correct towards the process of radical transfer. We estimated balances of OH radicals and H_2O_2 with the account of OH· dimerization reactions and OH· recombination with atomic hydrogen, so as OH· and H_2O_2 transfer to gas phase under ion bombardment. Contribution of transfer process to total destruction process of particles was found 0.05% for OH radicals and 4% for hydrogen peroxide.

The water transfer factor at glow discharge with electrolyte cathode was measured at on-line control of solution weight changes. The transfer factor increased during discharge burning, this growth being not determined by the increase of nonequilibrium evaporation contribution due to solution heating under discharge treatment. The transfer factor obtained was extrapolated to zero time of discharge burning. Its dependence on the anode–solution distance is presented in Figure 4. At stable discharge burning, the transfer factor grows with interelectrode distance. This fact allows us to explain the decrease of hydrogen peroxide yield observed under these conditions. Really, at the essential contribution of transfer process to the balance of OH radicals (as well as hydrogen peroxide) the increase of transport rate causes the decrease of dimerization contribution in expenditure of OH radicals. It results in the reduction of hydrogen peroxide accumulation due to an increase of its transfer to a gas phase.

As mentioned above, the transfer of solution components to a gas phase is accompanied by arising compensating flows in the solution volume. Our experiments showed that radial flows take place in solution from a cathode spot zone to peripheral areas. Thus, radial flows must be taken into account together with transfer processes in the balance of primary and secondary active particles generated in a cathode spot area. Thus, the total flow from bulk solution to a cathode spot will be equal to the sum of radial flows and the flow to a plasma zone. In our opinion, the rise of closed structure of flows in solution under glow discharge action can be explained as described below.

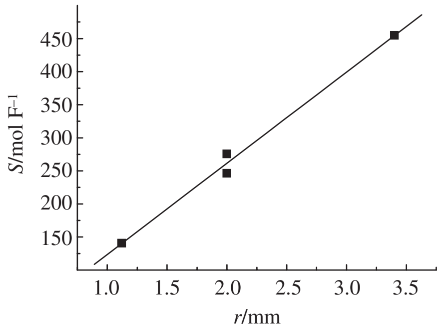

Figure 4 Dependence of the transfer number of solution components on discharge gap (0.01 M Na_2SO_4, 50 ml, 10 mA).

The cathode potential drop at a solution surface was about 500 V.[2] The thickness of a solution superficial layer where the energy of ions dissipates completely does not exceed 0.03 μm. Kutepov *et al.*[3] found that the density of energy scattered in superficial solution layer was enormously high (up to ~10^7 W cm^{-3}) at a small discharge current (10 mA), the diameter of a cathode spot was smaller than 3 mm. The solution can be considered nonequilibrium supercritical. It is responsible for the fact that average energy expenses for the transfer of water molecules to a gas phase is no higher than thermodynamically equilibrium ones (no more than 0.5 eV).

Rough estimations of energy balance in a cathode spot area show the translation energy of heavy particles in this area to be corresponding to a temperature of about 2000 K.[3] The time of particle contacts with the cathode spot area does not exceed 10 μs. In our opinion, the transfer of solution components to a gas phase is similar to MALDI, the transfer of big molecules dispersed in a matrix to a gas phase under laser irradiation.[5,6] This process is considered as the pulse evaporation of large clusters consisting of matrix molecules with bulky molecules dispersed among them. In our case, the solvent can be considered as a matrix with a dissolved substance dispersed among its molecules. Thus, we can consider transfer as a very fast evaporation accompanied by the transition of water clusters to a gas phase, with included the molecules of dissolved substance. Very fast heating of the solution falling to cathode spot area, naturally, results in its expansion in available (radial) directions. Thus, the energy dissipated in cathode spot area is consumed for kinetic energy of streams in liquid and gas phases. Our estimations on the basis of on-line video shootings with the use of a coordinate scale show the average rate of liquid in solution volume to be about ~1 cm s^{-1}. At the same time, the video shooting showed that only a small part of flows circulating in solution passes through the hot zone of a cathode spot. We assume the thickness of the superficial layer corresponding to the area of activated radial flow to be equal to the depth of penetration of primary ions in solution (~0.03 μm). Then the solution flow through cathode spot area is about ~10^{-6} mol s^{-1} (~6×10^{17} molecule s^{-1}), and that is essentially less than nonequilibrium evaporation flow.

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Received: 10th January 2007; Com. 07/2856