Possibility of producing hydrogen peroxide by cathodic reduction of oxygen

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The possibility of producing hydrogen peroxide by cathodic reduction of oxygen in solutions of potassium or sodium hydroxide was examined. It was shown that on porous cathodes prepared from commercial active carbons or from powdered electrographite, the current yields of hydrogen peroxide were nearly zero or too low for practical purposes. Further it was found that the current yields may be markedly enhanced by heating active carbon with sulfur compounds, *e.g.* potassium or sodium sulfide, before preparing the electrodes. Various dependences of current yields and cell voltage on the individual reaction conditions are given.

Была исследована возможность получения перекиси водорода катодическим восстановлением кислорода в растворах едкого натрия или калия. Было показано, что при применении пористых электродов из различных сортов активного угля или порошкообразного электрографита выходы по току почти нулевые или очень низкие для их технического использования. Далее было найдено, что выходы по току перекиси водорода возможно значительно повысить дополнительным обжигом активного угля с серными соединениями, напр. с сернистым калием, еще перед подготовкой пористых электродов. Далее приведены обнаруженые зависимости выходов по току и напряжения на ванне от различных условий режима работы.

Industrial methods of electrochemical production of hydrogen peroxide consist in anodic preparation of concentrated solutions of peroxodisulfuric acid or ammonium peroxodisulfate as intermediates, and in their subsequent hydrolysis at elevated temperatures and distillation of hydrogen peroxide under reduced pressure [1—3].

In spite of various improvements achieved during or after the World War II, these processes require a relatively large amount of electrical energy (10—13 kWh/kg H_2O_2 100%). For this reason, they began gradually to be replaced by more economical chemical autoxidation processes (*e.g.* the 2-ethylanthraquinone process) [1—4] especially in the case of large production capacities.

Hydrogen peroxide may, however, be obtained by another electrochemical process which is theoretically more economical than that proceeding *via* peroxodisulfates. The reaction consists in an incomplete cathodic reduction of oxygen to hydrogen peroxide

$$O_2 + H_2O + 2e \rightarrow O_2H^- + OH^- \qquad (1)$$

The standard reversible potential of the reaction (*1*) in an alkaline medium is $E^0 = -0.076$ V at 25°C [5]. Combining this reaction with the anodic evolution of oxygen (also in an alkaline medium) as the most simple anodic process, a cell with a theoretical standard reversible potential difference $E_{0,\mathrm{cell}} = 0.477$ V is obtained which is more than four times lower than the corresponding value for the peroxodisulfate formation. In spite of this advantage, this relatively old idea of producing hydrogen peroxide has not yet found any application in the industry, most probably due to the following reasons:

The main problem of the process consists in preparing cathodes with sufficiently long lifetime allowing to reduce gaseous oxygen to hydrogen peroxide with high current yields at sufficiently high current densities. From this point of view, most technical metals are unsuitable owing to their catalytic influence on the spontaneous decomposition of hydrogen peroxide into water and oxygen [6]. The only exception is mercury where oxygen is reduced in two well-developed waves [7]. It is, however, impossible to prepare a mercury cathode with a great specific surface area, and consequently the obtainable current densities are too low for practical use. A survey of papers dealing with unsuccessful efforts of preparing hydrogen peroxide by the reduction of oxygen on metallic electrodes is given in various handbooks [2, 3, 8].

The greatest progress in the research of the process was achieved in the thirties by *Berl* [9] and *Berl* [10], who used porous electrodes made from various carbonaceous materials, especially active carbon, to reduce oxygen to hydrogen peroxide. According to the papers mentioned and various patent applications [11, 12] not always technically realizable it was possible to prepare relatively high concentrated solutions of hydrogen peroxide (up to 25% H_2O_2) with high current yields (60—100% depending upon the reaction conditions) in solutions of potassium hydroxide as the starting electrolyte. Later, promising results were obtained by *Mizuno et al.* [13, 14] and by *Ignatenko* and *Barmashenko* [15], mostly in short-time experiments, and recently by *Kastening* and *Faul* [16]. In all the quoted papers, the possibility of a laboratory scale preparation of solutions of hydrogen peroxide by the cathodic reduction of oxygen in porous cathodes, made from active carbon, was presented. The process has, however, not yet been applied in the industrial practice. According to our opinion, the reason may lay in a low reproducibility of the properties of large surface carbonaceous porous electrodes, and especially in their short lifetime.

It follows from the dependences of the reversible potentials of the cathodic reaction (*1*) and the anodic oxygen evolution on pH [17], that the reversible cell voltage, $E_{r,\mathrm{cell}}$, in solutions with $\mathrm{pH} > 11.6$ (at 25°C) is lower than in acidic or neutral solutions (Fig. 1) due to the fact that in basic solutions hydrogen peroxide is present predominantly in the ionized form as anion O_2H^- It would be convenient

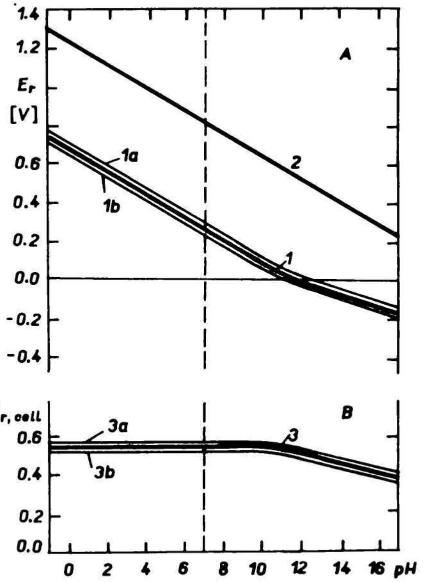

Fig. 1A. Dependence of reversible potential E_r on pH at 25°C for reaction (*1*) for $m_{O_2H^-} = 1$ (*1*); 0.1 (*1a*), and 10 (*1b*), and for reaction $2H_2O = O_2 + 4H^+ + 4e$ (*2*).

Fig. 1B. Dependence of reversible cell voltage $E_{r,cell}$ on electrolyzer with anodic oxygen evolution and cathodic reduction of oxygen to hydrogen peroxide at 25°C for $m_{H_2O_2} = 1$ (*3*), 0.1 (*3a*), and 10 (*3b*).

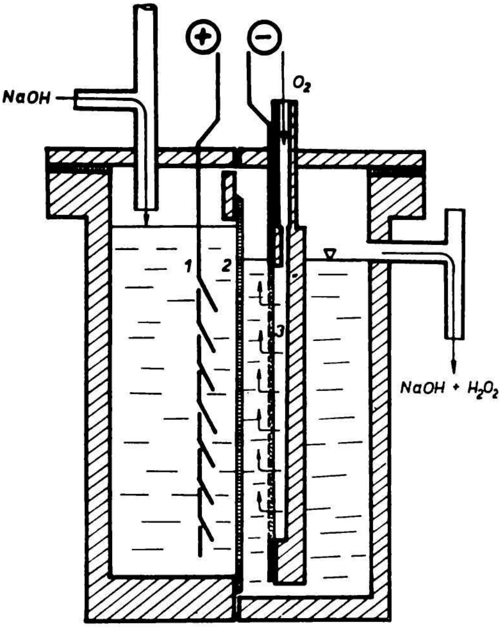

Fig. 2. Scheme of a laboratory scale flow electrolyzer for the preparation of hydrogen peroxide by cathodic reduction of oxygen in solutions of sodium or potassium hydroxides.
1. Anode; *2*. filtering diaphragm; *3*. porous cathode.

to work with starting solutions of sodium or potassium hydroxides of a maximum electrical conductivity (*ca.* 5 N–NaOH or 7 N–KOH at room temperature [18, 19]) leading to the lowest values of IR drops in the electrolyte and diaphragm. In the case of KOH, the use of such a concentrated solution causes no complications; as the content of hydrogen peroxide increases, the system remains in the region of unsaturated solutions. Using cheaper sodium hydroxide for the starting solution may, on the other hand, bring complications in the possible undesirable formation of sparingly soluble sodium peroxide, $Na_2O_2 \cdot 8H_2O$, in certain concentration regions [20], especially within the pores of the cathode. The problem of a more simple case of zero concentration gradients in a porous cathode was discussed in detail in our previous communication [21]. A more complicated case including the influence of concentration gradients of individual ions in the porous electrode will be the subject of a subsequent paper [22]. The present paper gives the results of experiments dealing with the mentioned process using porous cathodes made from various species of commercial carbonaceous materials in starting solutions of sodium or potassium hydroxides.

Experimental

Cell

All experimental data were obtained in a flow electrolyzer with a vertical filtering diaphragm made of porous PVC (Fig. 2). The anodic compartment contained a vertical anode made of a nickel sheet shaped as shown in Fig. 2, and a glass cooler for regulating the anolyte temperature. The cathodic compartment was arranged analogically. The porous cathode was prepared by spreading a suspension of the carbonaceous material together with the hydrofobing and binding agents in a mixture of benzene and xylene onto a fine nickel screen serving also as a mechanical support and current inlet [23]. The screen with the active layer was fixed to the frame of an acrylic glass holder through which oxygen was fed into the cathode. The starting solution flowed into the anodic compartment of the cell through a tube in the top, and after passing through the filtering diaphragm it flowed out as catholyte from the cathodic compartment through a tube placed 1 cm above the cathode frame.

The cell was loaded with constant current from a stabilized power source, the current being regulated by a resistor and measured simultaneously with the voltage of the cell. The desired flow rate was held by means of a micropump (Vývojové dílny, ČSAV). The temperature in both electrode compartments was measured by thin-wall glass thermometers.

Measuring

At first, the flow of gaseous oxygen was set in through the porous electrode and the electrolyzer was filled with electrolyte; after switching on the current and the electrolyte pump, the flow of oxygen was adjusted to the final amount twice exceeding the stoichiometric consumption given by eqn (*1*). On the cathode two side reactions were observed besides the reduction of gaseous oxygen to hydrogen peroxide (eqn (*1*)): the reduction of hydrogen peroxide to water and, at high cathodic potentials, the evolution of gaseous hydrogen. The excess of gaseous oxygen passed through the pores of the cathode into the catholyte in small bubbles, stirring the electrolyte and homogenizing it. The amount of the catholyte flowing out from the cathode compartment was measured and analyzed with respect to the content of hydrogen peroxide (permanganometrically). From these data the current yields of hydrogen peroxide were calculated.

Preparation of porous cathodes

Powdered carbonaceous materials were washed with distilled water, dried and mixed with a solution of smoked natural rubber in a mixture of benzene and xylene with paraffin added as hydrofobing agent. The suspension was spread in several layers onto a fine nickel screen. To compensate the influence of hydrostatic pressure on the flow rate of gaseous oxygen through the vertical porous system, the electrode was made thicker at the upper end. The geometric surface area of the square form electrodes was 60 cm^2, their average thickness was 0.3—0.5 mm.

Results and discussion

To verify Berl's data on the possibility of preparing porous electrodes from commercial active carbons without any further pretreatment for hydrogen peroxide formation by cathodic reduction of oxygen, we first made the electrodes of three commercial species: Carboraffin and Desorex (ČSSR), and SKT (USSR), fabricated by different activation processes. The first one was activated by $ZnCl_2$, the second one by steam [24], and the third one by potassium sulfide and steam [25]. Further experiments were made with electrodes prepared from powdered electrographite SE 86 (Elektrokarbon, Topoľčany). The results of the experiments

Table 1

Preparation of hydrogen peroxide by cathodic reduction of oxygen in porous cathodes made of various commercial species of carbonaceous materials without any further treatment

Carbonaceous material	Electrolyte	t °C	Flow rate cm^3/h	j_c mA/cm^2	t h	Current yields %	Cell voltage V	$c_{H_2O_2}$ g/l
Carboraffin	2 N-NaOH	20	30	17	18	0.0	1.93	0
Desorex	5 N-KOH	20	30	17	20	0.0	1.00	0
	5 N-KOH	20	30	17	35	1.7	1.00	0.37
SKT	2 N-NaOH	20	30	8.5	17	17	1.46	1.84
Electrographite SE 86	2 N-NaOH	20	30	0.85	22	29.9	1.18	0.32
	2 N-NaOH	20	30	0.85	47	16.1	1.24	0.17

are given in Table 1. As it is seen, during 18—35 h and at a reference current load 1 A, *i.e.* 17 mA/cm^2 of geometric area, the electrodes from Carboraffin and Desorex produced hydrogen peroxide with nearly zero current yields. On electrodes from active carbon SKT, the current yields were somewhat higher, though too low for practical use as well. The same may be said about the electrodes from powdered electrographite where, due to the lower specific area of the material, lower current densities were also used.

Such low current yields of hydrogen peroxide formation are obviously caused either by a lower activity of cathode material for the electroreduction of oxygen to hydrogen peroxide and, at the same time, a higher activity for the subsequent reduction of the primarily formed hydrogen peroxide to water and simultaneously for the spontaneous chemical decomposition of hydrogen peroxide, or just by a very low activity for the electroreduction of oxygen to hydrogen peroxide. In this case at the current densities used, practically only hydrogen is evolved on the cathode. The experimental data, however, do not supply sufficient information for a decision which of the proposed explanations is more probable one.

The results in Table 1 give evidence that the commercial powdered carbonaceous materials used without a further treatment are not suitable for the preparation of porous cathodes for producing hydrogen peroxide by the mentioned process, which is quite contradictory to *Berl* [9—12]. Further, the results show that there exist many factors in the process which have not been elucidated so far. This also explains the fact that although economically very promising, the process has not yet been brought to life.

It seems that for achieving higher current yields of hydrogen peroxide, it would be necessary to depress the natural catalytic activity of commercial carbons to its decomposition. We found that one way to reach this is to heat active carbon with some sulfur compounds, *e.g.* sulfides [26], before making the electrodes. The results of experiments made with porous electrodes from Carboraffin pretreated by this procedure under various reaction conditions are given in Figs. 3—7. Fig. 3 represents the dependence of current yields of hydrogen peroxide on the apparent current density in 1 N-NaOH (curves *1—4*) and 5 N-KOH (curve *5*) for an electrolyte flow of 50 cm^3/h. Individual curves *1—4* demonstrate the change of this dependence on time. The experimental data given by circles represent the average values for min. 24 h (mostly for min. 48 h); the direction in which the current densities varied successively is indicated by arrows. Curves *1—4* represent the time sequence in which the individual series of the dependence studied were examined. As it is seen from the position of curves *1—4*, the system gradually approaches a steady state which, however, was not completely achieved even after 823 h of all the four series. From Fig. 3 it follows further that the current yields still reach technically interesting values, especially in the range of lower current densities (10—40 mA/cm^2); the concentration of hydrogen peroxide changed in the range

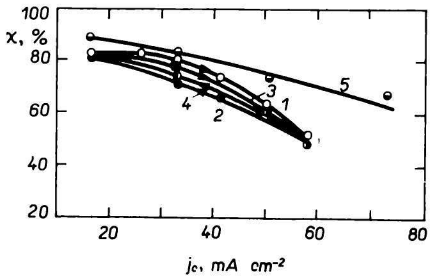

Fig. 3. Dependence of current yields χ of hydrogen peroxide on current density j_c for electrode No. 7 in 1 N-NaOH (curves *1*—*4*), and for electrode No. 6 (curve *5*) in 5 N-KOH, at flow rate of 50 cm^3/h at 10°C.

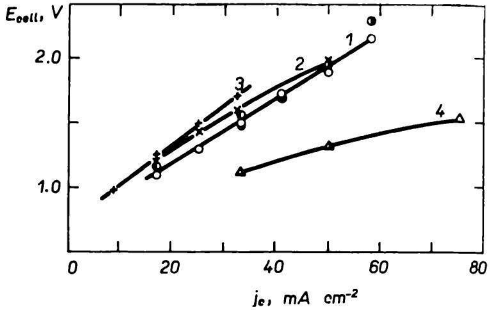

Fig. 4. Dependence of cell voltage E_{cell} on current density j_c for electrode No. 7 (*1*) and 12 (*2*) in 1 N-NaOH and electrode No. 7 (*4*) in 5 N-KOH at flow rates 50 cm^3/h, and electrode No. 12 in 1 N-NaOH at flow rate 30 cm^3/h (*3*).

0.3—2 M according to the reaction conditions used. It is also evident that the decrease of current yields with increasing current densities is affected by the nature and concentration of hydroxide.

The dependence of the cell voltage on the current density is shown in Fig. 4. Here, the direct line *1* corresponds to the same experiments as expressed by curves *1*—*4* in Fig. 3, curve *2* gives the dependence for another electrode at the same reaction conditions, curve *3* shows an analogical dependence for the case of a flow rate of 30 cm^3/h, and curve *4* expresses the dependence for 5 N-KOH (it corresponds to curve *5* in Fig. 3).

The influence of temperature on the current yields and on the cell voltage for the same reaction conditions for an electrolysis in 1 N-NaOH is shown in Fig. 5. It may be seen that an increase of temperature from 10 to 20°C causes a decrease of current yields of approximately 8% irrespective of the current density. On the other hand, the rising temperature causes — according to expectations — a decrease of the total cell voltage by approximately 60 mV for this temperature difference, also irrespective of the current density.

The current yield of hydrogen peroxide is further considerably dependent on the flow rate of the electrolyte through the cell (at a given current density) which influences the total hydrogen peroxide concentration in the outflowing catholyte as well. The dependence of current yields on both these quantities is shown in Fig. 6 from which it may be seen that the current yields decrease rapidly with increasing concentration of hydrogen peroxide in the final solution, or with a decrease in the flow rate of the electrolyte through the cell. Converting the results shown in Fig. 6 into the dependence of current yields on the time delay of catholyte in the cathodic compartment we can obtain the relation presented in Fig. 7; it shows that the current yields of hydrogen peroxide decrease almost linearly with the time delay of catholyte in the cathodic compartment.

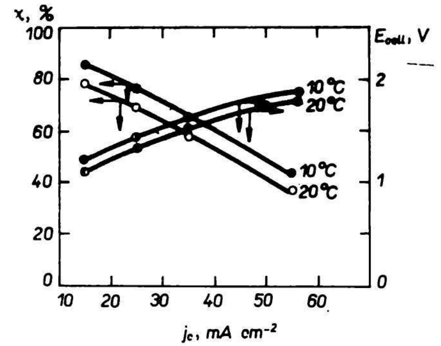

Fig. 5. Dependence of current yields χ and cell voltage E_{cell} on current density j_c for electrode No. 12 in 1 N-NaOH and flow rate 50 cm^3/h at 10 and 20°C.

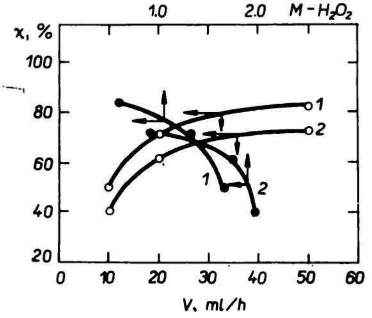

Fig. 6. Dependence of current yields χ of hydrogen peroxide on flow rate of electrolyte (○) or the corresponding hydrogen peroxide concentration (●) for electrode No. 6 in 5 N-KOH and current density 33 mA/cm^2 (*1*) and 50 mA/cm^2 (*2*), respectively, at 10°C.

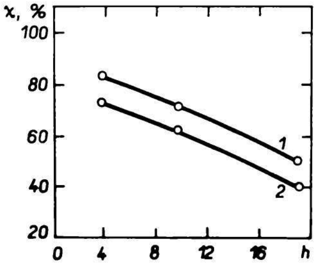

Fig. 7. Dependence of current yields χ of hydrogen peroxide on time delay of catholyte in the cathodic compartment for electrode No. 6 in 5 N-KOH and current density 33 mA/cm^2 (*1*) and 50 mA/cm^2 (*2*) at 10°C.

The results of the last two figures testify that the decrease of current yields with increasing concentration of hydrogen peroxide in the outflowing catholyte is caused by these factors: a) the increasing rate of the spontaneous hydrogen peroxide decomposition; b) the increasing transfer number of perhydroxyl anion O_2H^- migrating from the cathodic into the anodic compartment; c) the influence of the increasing concentration of the reaction product on its formation rate.

The results achieved indicate the possibility of a modification of commercial active carbons for the preparation of porous cathodes allowing to produce hydrogen peroxide by cathodic reduction of oxygen with sufficiently high current yields. A more detailed quantitative examination of these relations will be the subject of further investigations.

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