

**PREPARATION OF HYDROGEN PEROXIDE
BY CATHODIC REDUCTION OF OXYGEN
IN POROUS ELECTRODES MADE
OF DIFFERENT CARBONACEOUS MATERIALS**

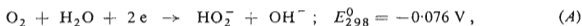
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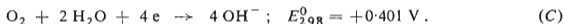
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The rate of formation of hydrogen peroxide by cathodic reduction of oxygen in porous electrodes made of natural graphite, electrographite, carbon black and active carbon has been studied, as well as the catalytic effect of these materials on spontaneous decomposition of alkaline solutions of hydrogen peroxide. The measured data revealed that the greatest current yields of hydrogen peroxide were attained with electrodes made of low-surface kinds of carbon black which simultaneously had the lowest catalytic effect on the spontaneous decomposition of hydrogen peroxide.

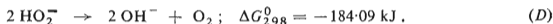
Cathodic reduction of oxygen can proceed, according to the character of electrode material and the reaction conditions, either in two consecutive two-electron steps which can be, *e.g.* for alkaline medium, expressed by equations



or as a direct four-electron reaction, described by the overall equation



Two-electron reduction of oxygen according to reaction (A) proceeding under the formation of hydrogen peroxide as a relatively stable intermediate, takes place *e.g.* on mercury and on some carbonaceous materials^{1,2}. Direct four-electron reduction according to overall Eq. (C) is known to proceed, at least in part, on electrodes made of noble metals (Pt, Au, Rh)³⁻⁶. The primarily formed hydrogen peroxide, or the perhydroxyl anion, however, is not a thermodynamically stable product and therefore it can spontaneously decompose to form again gaseous oxygen and water or hydroxyl ions according to the overall equation (again written for alkaline medium)



This, from the point of view of hydrogen peroxide preparation, unwanted decomposition reaction is considerably catalyzed by various both homogeneous and heterogeneous catalysts, present in the reaction system.

Berl^{2,7} was the first to make use of the ability of some kinds of active carbon to reduce oxygen to hydrogen peroxide at technically applicable current densities for the purpose of hydrogen peroxide preparation. However, in spite of the great effort in this field, all attempts to realize this economically very promising process failed. Nevertheless, its practical application remains in the centre of attention⁸⁻¹¹.

In our previous communications¹² we have published the results of attempts to prepare hydrogen peroxide *via* the above mentioned procedure using porous electrodes made of differently treated active carbon. The reason was that porous cathodes of non-treated commercial types of active carbon were found to produce hydrogen peroxide in low yields, so that special processes of treatment were necessary to increase the yields¹¹⁻¹³.

The present publication brings the results of continued studies of preparation of hydrogen peroxide by reduction of oxygen in porous electrodes prepared of further kinds of powdered carbonaceous materials (natural graphite and electro-graphite and different types of carbon black), attempting to find suitable materials for the preparation of porous cathodes which might produce hydrogen peroxide in the range of technically acceptable current densities, in sufficiently high current yields and without any further expensive treatment of electrode materials.

With respect to the fact that the reaction rate on a porous electrode depends to a great extent on its structure, we have carried out, in addition to the preparative electrochemical experiments, also measurements of the porous structure of the electrodes used. Further we have measured the catalytic activity of the used electrode materials for spontaneous decomposition of alkaline solutions of hydrogen peroxide as well as the physical surface area of these materials.

EXPERIMENTAL

Preparation of electrodes and working procedure. Whereas the earlier employed method of preparation of porous electrodes consisted in spraying a suspension of active carbon in benzene-xylene mixture, containing a certain amount of dissolved raw rubber¹², onto a dense nickel screen, in the present work the porous electrodes were prepared by mixing water suspension of the studied carbonaceous material (grain size less than 50 μm) with a teflon dispersion (Fluon GP 1) in such a ratio that the content of teflon in dry electrode was 5 mass%. The stirred suspension was filtered off, the filter cake was washed several times with distilled water, dried, pulverized and pressed under *c.* 30 MPa into a circular plate of 3.1 cm diameter. The nickel network was pressed to one side of the disc and a porous teflon foil to the other side. The so prepared porous electrode was 0.6–0.8 mm thick and contained *c.* 50 mg of active mass per 1 cm^2 . For measuring the stationary polarization curves of oxygen reduction the electrode was fitted into the electrolyzer by means of a suitable holder with oxygen input and electric current supply in such a position that the nickel screen was facing the electrolyte. Oxygen was fed into the electrode under 2.67 kPa overpressure (20 mm Hg). Nickel screen served as anode and the cathodic compartment was separated from the anodic one by the filtering polyvinylchloride diaphragm PORVIC. The electrolyte was fed into the anodic compartment at a constant rate 15 ml/h, flew through the filtering diaphragm and was collected on leaving the cathodic compartment. The catholyte was analysed

manganometrically as to the content of hydrogen peroxide which served for evaluation of the current yields. 5M-KOH prepared from reagent grade potassium hydroxide and distilled water was used as electrolyte. The studied electrode was polarized potentiostatically using a potentiostat Wenking 68 FR 0.5, the minimum polarization time at a given potential being 20–25 h, whereafter the respective current was read off, serving to construct the stationary polarization curve. The measurement was usually carried out from the open-circuit potential of the system towards more negative potentials and in some cases the polarization curves were again measured in the reversed direction. Hg/HgO-electrode in the solution used as the starting solution for electrolysis (without O_2H^-) served as reference electrode. The measured potentials were then recalculated with respect to the equilibrium potential of hydrogen electrode in the same solution (RHE) and these values are given throughout the whole work. All measurements were carried out at $20 \pm 0.1^\circ C$.

The surface area of the studied carbonaceous materials was measured using the BET method. Distribution of pores in the prepared porous electrodes was determined by mercury porosimetry.

The decomposition rate of hydrogen peroxide in alkaline solutions in the presence of the studied carbonaceous materials was determined by measuring the volume of evolved oxygen. 0.1 g of the powdered carbonaceous material was mixed in a flask with 5 ml of distilled water and the suspension was heated to boil, until the surface of all particles became well wetted with water. After cooling, the suspension was treated with 5 ml of 10M-KOH. The mixture was tempered to $20^\circ C$ and further 10 ml of the tempered solution containing 5M-KOH and 1 ml 25M- H_2O_2 were added into the flask. The reacting mixture, as well as the evolved oxygen, taken in a gasometric burette, were continuously maintained at $20^\circ C$.

RESULTS AND DISCUSSION

Specific surface areas of the used carbonaceous materials are presented in Table I. From the given values it is evident that specific surface areas of the studied materials differed from each other by up to three orders of magnitude. Porosimetric curves of several electrodes made of the described materials are shown in Fig. 1. As can

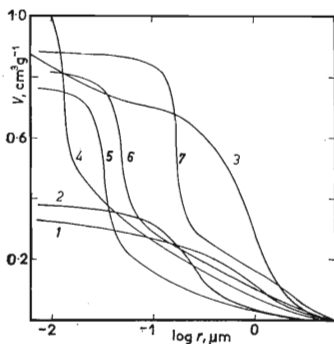


FIG. 1
Porosimetric Curves of Porous Electrodes
Made of Different Materials Studied
1 Electrographite, 2 natural graphite,
3 active coal untreated, 4–7 carbon black
I–IV.

be seen, electrodes made of electrographite have a rather small pore volume. Electrodes of carbon black contain mostly pores of the same size, ranging according to the type of carbon black from some hundredths to some tenths of μm . In contrast to these materials, electrodes made of active carbon contain high amounts of macropores of the radius *c.* $1 \mu\text{m}$ and micropores and transient pores with the radius of the order $10^{-3} - 10^{-2} \mu\text{m}$.

In measuring the decomposition of alkaline solutions of hydrogen peroxide in the presence of the studied materials for the preparation of porous electrodes it was found that in the given experimental arrangement the rate of oxygen evolution during the first half an hour to one hour is almost constant. The results of measurements in this time interval served to evaluate the rates of decomposition of hydrogen peroxide, expressed as the volume of gaseous oxygen evolved in unit time, and related to 1 g of the studied carbonaceous material, v ($\text{ml min}^{-1} \text{g}^{-1}$) or to 1m^2 of the physical surface area, v' ($\text{ml min}^{-1} \text{m}^{-2}$). The total measured decomposition rates, however, include not only the decomposition caused by the present carbonaceous material, but also the decomposition in the bulk phase of the electrolyte as well as the decomposition on the walls of the reaction vessel. In order to eliminate the latter two effects, we have measured, under identical reaction conditions, also the decomposition rate of hydrogen peroxide without addition of carbonaceous materials and this value was subtracted from the measured data. These corrected rates of decomposition of hydrogen peroxide by carbonaceous materials alone are summarized in Table I. From the results it is evident that both studied types of active carbon

TABLE I

Specific Surface Areas of the Studied Carbonaceous Materials and the Rates of Spontaneous Decomposition of Hydrogen Peroxide in the Medium of 5M-KOH Caused by the Presence of These Materials in the Reaction System, at 20°C

Carbonaceous material	Specific surface area, $\text{m}^2 \text{g}^{-1}$	Decomposition rate of H_2O_2	
		v $\text{ml min}^{-1} \text{g}^{-1}$	$v' \cdot 10^2$ $\text{ml min}^{-1} \text{m}^{-2}$
Natural graphite	9.8	0.60	6.12
Electrographite	6.1	0.58	9.12
Carbon black I	135	2.82	2.09
Carbon black II	34.7	0.94	2.71
Carbon black III	55.5	0.48	0.86
Carbon black IV	9.7	0.01	0.1
Active carbon	1 200	59	4.92
Active carbon	1 090	21.3	1.95

have an extraordinarily high catalytic activity in the decomposition of hydrogen peroxide. This effectiveness is obviously especially due to their very large surface area. Also the concentration of surface oxygen containing groups (or unpaired electrons), which are considered as the centers of the decomposition of hydrogen peroxide^{12,14}, can play an important role. On the other hand, some types of carbon black, particularly those with small specific surface area (carbon black IV) were found to accelerate only very slightly the spontaneous decomposition of hydrogen peroxide according to Eq. (4), which is documented by the decomposition rates v' related to 1 m^2 of the surface. From these results it can be concluded that this kind of carbon black could be a suitable material for the economical preparation of porous electrodes for hydrogen peroxide production.

The validity of these assumptions is confirmed by the results of measurements of stationary polarization curves of oxygen reduction on electrodes made of the studied materials, as shown in Fig. 2. It was ascertained that when the electrodes were polarized in the potential region 0.6–0.8 V, the total current densities did not undergo any practical change with the time of polarization in the interval 20–25 h, or they slightly increased. At more negative potentials a more or less fast decrease of current densities was observed. This phenomenon is manifested on some polarization curves (curves 2, 4 and 5 in Fig. 2) even as a final decrease of cathodic current

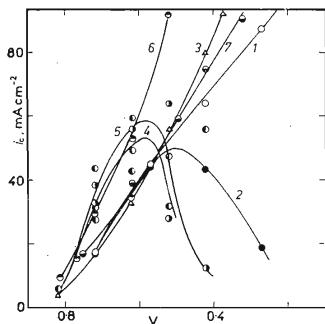


FIG. 2

Total Polarization Curves of Oxygen Reduction in Porous Electrodes Made of Different Carbonaceous Materials, in 5M-KOH at 20°C

Numbering of curves and materials the same as in Fig. 1.

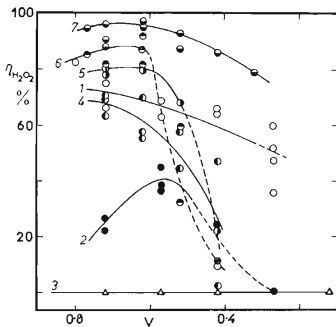


FIG. 3

Dependence of Current Yields of Hydrogen Peroxide on the Potential of Porous Cathode in the Reduction of Oxygen in Porous Electrodes Made of the Studied Carbonaceous Materials, in 5M-KOH at 20°C

Numbering of curves and materials the same as in Fig. 1.

densities with simultaneous shift of potential to more negative values. The cause of this phenomenon was obviously the flooding of the gas pores of the electrode and consequently the decrease of the length of the three-phase interface, on which the studied reaction takes place. When no protective porous teflon foil was attached to the gas side of the electrode, the formation of drops occurred on the gas side of the electrode, or even flowing of electrolyte through the electrode. When the "flooded" electrode was washed with distilled water, dried and again put into service, it showed approximately the same electrochemical activity, of course the current decrease with time was faster in this case. This finding can be explained so that the surface area of pores, wetted in the preceding polarization, is already slightly oxidized by the peroxide ions from the electrolyte and thus it is more hydrophilic, than in the first polarization. Also the greater scattering of points on the total polarization curves 4 and 5 in Fig. 2, which were measured after various times of preceding polarization of electrodes at different potentials, can be explained by the flooding of electrodes. This result demonstrates the great dependence of current densities on potentials as well as on the time of preceding polarization of electrodes.

The flooding of gas pores of the electrode at more negative potentials is evidently brought about by the change of the interface tension in the system electrode material–electrolyte–gaseous oxygen, wherein a certain role is also played by the gradual oxidation of the surface of the electrode material by the formed hydrogen peroxide whose concentration in the sites of its formation is rather high.

Comparison of the polarization curves of electrode made of active carbon with other electrodes brings a rather interesting knowledge that total current densities are not in direct relation with the total size of the physical surface area of the electrode material. This result shows that the reduction of oxygen to peroxide proceeds similarly as its total reduction in porous electrodes of fuel cells^{15,16} prevailing in the vicinity of gaseous macropores. The internal surface of micropores, that has the determining effect on the total physical surface area of the electrode, does not practically take part in the electrode reaction.

The dependence of current yields of hydrogen peroxide on the potential of electrodes made of different carbonaceous materials used in this study is shown in Fig. 3. As can be seen, in contradiction to the total current densities, the current yields of peroxide depend very distinctly on the type of carbonaceous material of the porous electrode. Practically no hydrogen peroxide was formed on the electrode made of untreated active carbon, which is also in accordance with the results of previous measurements¹² and also with the high catalytic activity of this material in the spontaneous decomposition of peroxide (Table I). The current yields of peroxide on electrodes made of carbon black are the higher the lower is the decomposition activity as related to the mass of this material.

Another important finding followed from Fig. 3, namely that at potentials more negative than *c.* 0.6–0.5 V (RHE) the current yields of hydrogen peroxide decrease

on all kinds of porous electrodes. This decrease is obviously caused on the one hand by the beginning reduction of the primarily formed peroxide (according to the overall Eq. (B)), on the other hand by the gradual flooding of the gas pores of the electrode, as already mentioned above. This results in an increase of the portion of flooded internal surface of the porous electrode which can catalytically affect the spontaneous decomposition of hydrogen peroxide. Consequently, the amount of peroxide ions, decomposed in the electrode, increases, which is manifested outwards by a further decrease of its current yields. In the cases when total flooding of the electrode took place, the current yields of hydrogen peroxide dropped down to only a fraction of the original value. The observed decrease of current yields of hydrogen peroxide is very important for its proper preparation by the described procedure, since it delimits the regions of potential in which it is possible to work with sufficiently high current densities, whereby both high current yields and the lowest danger of flooding of gas pores of the electrodes¹⁶ are provided.

According to the results of measurements, the most suitable electrode material for the preparation of alkaline solutions of hydrogen peroxide by cathodic oxygen reduction appears to be carbon black IV, on which the current yields of peroxide in the potential region 0.8–0.5 V (RHE) amounted over 90% wherein the current density, corresponding to the respective values of cathodic potential, lay in the interval 10–60 A/cm². It was demonstrated by further measurements that the electrochemical activity of these electrodes did not decrease even after hundreds of hours of polarization. Thanks to the low decomposition activity of the studied carbon black this electrode produces hydrogen peroxide with almost unchanged yields even at concentrations up to 70 g H₂O₂ per liter, *i.e.* up to 2M. Thus the results obtained demonstrate that some kinds of carbon black represent a suitable material for the preparation of porous electrodes, producing hydrogen peroxide with high current yields in the region of technically interesting current densities, and, moreover, this material need not be additionally treated by relatively expensive procedures¹⁷. The measurements also confirmed that untreated active carbon is entirely unsuitable for the preparation of hydrogen peroxide by the described procedure. Good results with electrodes made of active carbons can evidently be attained only using additional special treatment of such materials to decrease their high catalytic activity in the spontaneous decomposition of the formed hydrogen peroxide^{11,13}.

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