POROUS ELECTRODES FOR HYDROGEN PEROXIDE PREPARATION BY OXYGEN REDUCTION. THE INFLUENCE OF TEMPERATURE AND PRESSURE APPLIED IN PREPARATION OF THE ELECTRODES ON THEIR FUNCTIONAL PROPERTIES

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The influence of the temperature and pressure applied in preparation of porous electrodes from Teflon-bonded carbon black on the hydrogen peroxide current yield and the current density was investigated. The porous structure, the wetted surface area of carbon black, and the electric resistance of the electrode mass were examined in order to establish the factors responsible for the varying electrode activity.

It is well known that the electrochemical properties of gas diffusion electrodes made of metal powders or carbonaceous materials depend not only on the kinds and contents of the electroactive material and the hydrophobic agent, on the internal surface area or the particle size of the two main components, but also on the preparation conditions which affect the porous structure of the electrodes. For example, a temperature increase in the sintering of Teflon-bonded electrodes was found to result in a decrease of the electric resistance of the electrodes, and simultaneously in a rise of the current density of oxygen reduction[1,2]. For electrodes made of active carbon with an addition of silver, Mrha and coworkers[2] found that the current density decreased as the pressure applied in preparing the electrodes had been increased. This observation was explained in terms of enhancement of transport hindrance with a decrease in the electrode porosity.

So far published papers on gas diffusion electrodes for oxygen reduction are mostly concerned with fuel-cell electrodes at which four-electron oxygen reduction takes place. These electrodes are usually made of a hydrophilic material (silver powder, platinum powder, active carbon, *etc.*) that is sufficiently active for the peroxide decomposition, and a hydrophobic agent which acts simultaneously as a binder. On the other hand, the electrodes used to prepare alkaline solutions of hydrogen peroxide by incomplete oxygen reduction according to the overall equation

$$O_2 + H_2O + 2e \rightarrow HO_2^- + OH^- \qquad (A)$$

have different composition and properties[3-5]. The present work deals with the relation between structural and electrochemical properties of electrodes of the latter type containing highly hydrophobic carbon black as an active material, and Teflon as a hydrophobic binder.

EXPERIMENTAL

Electrode preparation. Furnace black of small specific surface area and low activity for hydrogen peroxide decomposition was mixed with distilled water. A Teflon (Fluon GP 1) dispersion was then added dropwise to the suspension with continuous stirring, in an amount corresponding to 12 wt % PTFE in the dry mixture. The solid phase was filtered off, washed several times with distilled water, and dried at 120°C. After disintegration, the mixture was spread on a nickel screen, and pressed under 20 MPa. The resulting flexible plate of 31 mm diameter and 0·8—1 mm thickness contained about 70 mg of the dry mixture per 1 cm^{-2}. Three types of electrodes were prepared: *I.* "Cold-pressed" electrodes, by applying the above described procedure; *II.* "Sintered" electrodes, by additional heating of electrodes *I* in air at 380°C for 30 min; *III.* "Hot-pressed" electrodes, by additional pressing of electrodes *I* at 20 MPa and 350°C for 2 min.

The electrode was fixed in an acryl holder providing oxygen input and electric current supply into the electrode[4,5]. The effective geometrical surface area of the cathode was 5·7 cm^2. The oxygen electrode was placed in a laboratory-scale continuously working flow-through electrolyzer with a filtering diaphragm, where oxygen was evolved at a nickel anode.

Hydrogen peroxide current yields were evaluated from the peroxide content of the electrolyte leaving the cathodic compartment, the catholyte flow rate, and the total current passing through the electrolyzer under stationary conditions. The measurements were performed at 20°C, mostly at potentiostatic conditions. The electrode potential was measured against a reference Hg/HgO electrode in a hydroxide solution of the same concentration as that at the electrolyzer input. All potential values in this paper are related to this reference electrode. Further experimental conditions have been described in greater detail in a previous paper[4].

The wetted surface area of electrodes was determined from the electrode capacity in a double-layer region from 0·2 to 0·45 V (R.H.E.) (ref.[6]). The electrode capacity was evaluated from the cathodic and anodic charging curves measured at very small current densities (10^{-9} to 10^{-8} A/cm^2 of the BET internal surface area of carbon black). The charging curves were measured in pure 5M-KOH solution through which oxygen-free argon or nitrogen had been bubbled for about 12 h to remove dissolved oxygen. In order to determine the specific capacity of the wetted surface area of carbon black, the described measurement was first performed on the carbon black alone. Prior to the measurement, the carbon black was evacuated to improve its wetting. The specific capacity of the wetted surface area of carbon black, calculated from the measured capacity and the BET surface area of carbon black, was found to be 12 μF cm^2. This result fits into the range found by Mokrousov and coworkers[6] for various sorts of carbon black

TABLE I

Specific resistance and density of electrodes

Electrode type	Specific resistance Ω cm	Density g cm^{-3}
I	1·64	0·72
II	1·58	0·74
III	0·78	0·83

(10—15 $\mu F\ cm^{-2}$). The porous electrode capacities per unit internal surface area of carbon black, and the above given value for the completely wetted surface area were used to calculate the wetted surface area of porous electrodes after various times of their operation.

The amount of electrolyte in the pores of electrodes was determined by weighing. The total volume of pores was calculated from the electrode volume, the dry electrode weight, and the contents and densities of the electrode components. The electrode was submerged in 5M-KOH solution for various times, then wiped and weighed. The weight gains of the electrode were used to calculate the fractions of flooded pores.

The electric resistance of electrodes was measured by the four-electrode method[5] on samples without nickel screen.

RESULTS AND DISCUSSION

First, the influence of the method of electrode preparation on the specific electric resistance of the electrode mass was evaluated. The results (Table I) indicate that heating at 380°C at atmospheric pressure does not produce any appreciable change in the electrode resistance. The small change observed may be ascribed to a slight increase of the density of the electrode mass. It is only sintering of the electrodes under pressure that gives rise to a substantial decrease in the resistance. The specific resistances of electrodes of all types involved are so small, however, that the voltage

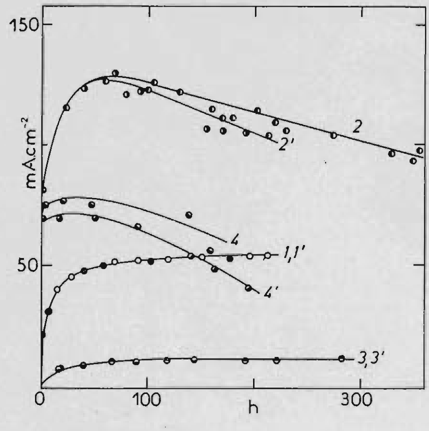

FIG. 1

Dependence of current density on time of polarization at a potential of —0·3 V for various types of electrodes: *1,1'* type I; *2,2'* type II; *3,3'* type III; *4,4'* type III with an addition of $KHCO_3$ (35 wt %)

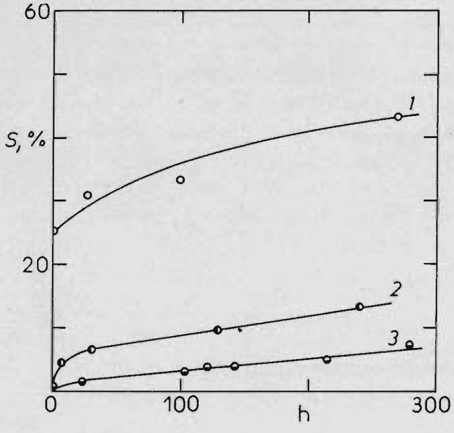

FIG. 2

Dependence of the degree of wetting of surface area of carbon black electrodes on time of polarization at a potential of —0·5 V: *1* type I; *2* type II; *3* type III drops across the electrode in the direction perpendicular to the electrode plane are insignificant at the current densities attained (*e.g.*, for an electrode of 1 mm thickness, a maximum voltage drop of 8 mV may occur at a current density of 50 mA/cm^2). On the other hand, the resistance of the electrode mass is not low enough to allow the electrodes to be used without a current collector (nickel screen).

Fig. 1 shows the variation of the current density with time for various types of electrodes polarized at a potential of $-0{\cdot}3$ V. The considerably higher current densities observed with the sintered electrodes(II) as compared to the current densities attained with the cold-pressed electrodes (I) might be explained either by an enhancement of the electrochemical activity of carbon black due to its heating in air, or by a change in the electrode wettability resulting in a more favourable distribution of liquid and gas phases within the electrode. In order to decide which of these explanations is valid, we performed an experiment comprising heating the carbon black in air at 380°C for 30 min, mixing it with Teflon, and cold-pressing the mixture to form an electrode. It was found, however, that the rate of oxygen reduction on such an electrode was the same as on electrodes made of thermally unpretreated carbon black.

On the other hand, considerable differences were found in the wettability of cold-pressed (I) and sintered (II) electrodes. The electrode weight gains after various times of immersion in 5M-KOH indicated that pores of cold-pressed electrodes were much more liable to wetting than pores of sintered (II) and hot-pressed (III) electrodes; *e.g.*, immersion for 150 h resulted in filling 7–11% of the pore volume of type I electrodes with the electrolyte whereas with electrodes II and III the filled pore volume was only 0·7 to 0·8%. Substantially greater flooding of the electrode pores occurred during the cathodic polarization: at a potential of $-0{\cdot}5$ V, 30 and 23% of the pore volume was found to have been flooded in electrodes of type I and II, respectively.

In order to assess the effect of electrode wetting on the current-carrying ability, the wetted surface area of porous carbon-black electrodes was measured, first with the electrodes placed in a cell at zero applied current and fed with an inert gas. After immersion for 6 h, 25% of the cold-pressed electrode surface area while only 0·5% of the thermally treated electrode (types II and III) surface area was found to have been wetted. The electrodes were then polarized at a potential of $-0{\cdot}5$ V under oxygen. The time dependences of the surface wetting are shown in Fig. 2. It can be seen from the figure that the extent of electrode wetting rises during the whole time of polarization, and that cold-pressed electrodes are substantially more wetted than thermally treated electrodes (II and III). The difference can be explained as the result of the decomposition of an emulgator from the Teflon dispersion during the thermal treatment of electrodes of type II and III.

During the above experiment, current densities and current yields of hydrogen peroxide were measured. It can be seen from Fig. 3 that at the beginning the current density goes up fairly rapidly, in proportion to the extent of electrode wetting. It is noteworthy that maximum current densities are reached at relatively small extent of wetting of the electrode surface (5 to 8 percent). As the fraction of the wetted surface area further increases with continuing polarization, the current density begins to decrease. This behaviour is caused either by an enhancement of transport hindrance in the gas phase or by a decrease in the electroactive material utilization due to enlargement of the flooded surface. The decrease of the current density of oxygen reduction is the faster the more negative is the polarization potential. At a potential of −0·3 V, the current densities at the sintered (II) and hot-pressed (III) electrodes reached nearly steady values after several tens of hours, which remained virtually constant for further several thousand hours of operation. At potentials within the range −0·7 to −1 V, however, total flooding of the electrode and a decrease in the current density to a small fraction of the initial value occurred after as little as few tens of hours of operation.

The enhancement of the wetting rate of porous electrodes with decreasing potential has been observed by several authors[7,8], and explained in terms of isothermal distillation of water which occurs as a result of the electrolyte concentration gradients within the electrode pores[8,9].

It is rather difficult to interpret the considerable differences observed in oxygen reduction rates at electrodes prepared by different methods. The higher current

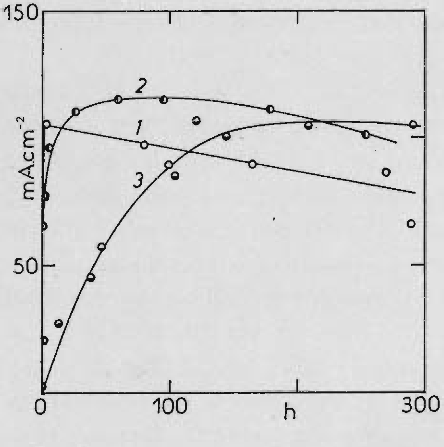

FIG. 3

Dependence of current density on time of polarization at a potential of −0·5 V. The curves and points are marked as in Fig. 2

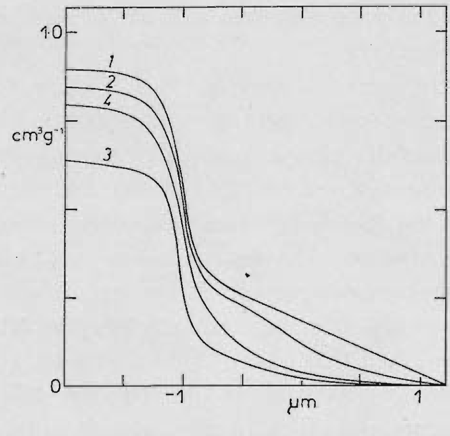

FIG. 4

Porosimetric curves for various types of electrodes: *1* type I; *2* type II; *3* type III; *4* type III with an addition of $KHCO_3$ (35 wt %)

densities on the sintered electrodes (II) as compared with the cold-pressed electrodes (I) may most likely be attributed to less transport hindrances in the electrode gas pores. Unlike what one might have expected, the wetting rates, and consequently also the current densities of oxygen reduction, were found to differ for the sintered (II) and hot-pressed (III) electrodes. As these differences could be explained by different pore structure of both types of electrodes, the pore size distribution was determined by mercury porosimetry. The porosimetric curves (Fig. 4) indicate that the content of large pores in the hot-pressed electrodes (III) is lower than in the cold-pressed (I) and sintered (II) electrodes (*e.g.*, the content of pores larger than 0·1 μm in diameter is reduced by a factor of about 2).

The influence of the pore size on the current density of oxygen reduction was investigated using an electrode prepared from a carbon black-Teflon mixture with an addition of 35 wt % of $KHCO_3$ of particle size up to 50 μm. The added carbonate decomposed during the hot-pressing to form CO_2 and K_2CO_3 which was then dissolved in distilled water. The resulting electrode contained about twice the amount of pores larger than 0·1 μm, compared with the electrode compressed without an addition of the porosity-increasing material. In accord with the assumption regarding the effect of large pores, the initial increase of the current density on this electrode occurred more rapidly than on hot-pressed electrodes without the porosity-increasing component (see curves *4* and *4′* in Fig. 1). Moreover, the more rapid wetting of the modified electrode was reflected also in subsequent faster decrease in the current density. These results confirm indirectly that large pores (greater than 0·1 μm) are the first to be filled up with electrolyte in the electrodes under study.

The method of electrode preparation was found to have little effect on the current yield of peroxide at potentiostatic conditions of polarization. At −0·3 V, the yields

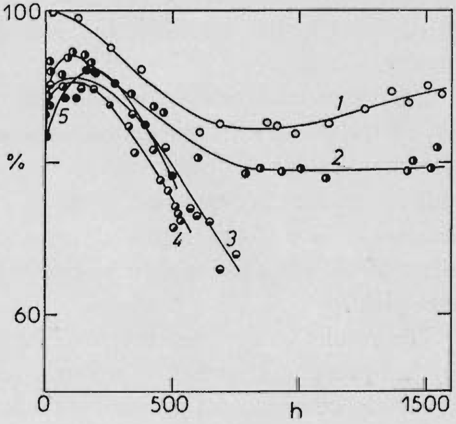

FIG. 5

Dependence of current yield of hydrogen peroxide on time of polarization at a current density of 50 mA cm^{-2} for electrodes hot-pressed under different pressures (MPa): *1* 0; *2* 0·28; *3* 3·5; *4* 10; *5* 22·5 were in the ranges 85–96%, 90–100%, and 80–90% for cold-pressed, sintered and hot-pressed electrodes, respectively. It may therefore be stated that the current yield was the higher the higher was the current density, which is in agreement with theoretical results on peroxide-producing porous electrodes[10].

Substantially larger differences may be encountered with galvanostatistically polarized electrodes where the potential of less electrochemically active electrodes decreases to more negative values (below −0·6 V) at which electrochemical reduction of hydrogen peroxide starts to play a role[11], resulting in a significant reduction of the current yield of the peroxide.

The results of our investigations would point to the electrodes sintered at atmospheric pressure (II) as having the best electrochemical parameters for the preparation of alkaline solutions of hydrogen peroxide. However, the mechanical strength of these electrodes is markedly inferior to that of hot-pressed electrodes (III). The influence of the pressure applied in electrode preparation on the electrochemical properties of electrodes was investigated using a number of electrodes sintered at pressures within the range 0 to 22 MPa. When polarized by a current density of 50 mA/cm^2, all the electrodes exhibited very negative initial potentials (ranging from −0·6 V to −0·8 V). The subsequent potential shift to the region favourable for peroxide formation (more positive than −0·6 V) lasted only about 10 min with the sintered electrode (II) while with the hot-pressed electrodes the duration was several tens of hours. During prolonged operation for 600 to 4 250 h, the electrode potential varied within the range −0·35 to −0·54 V.

With all the electrodes, there was an initial increase in the current yield of peroxide due to a positive shift of the cathode potential, followed by a slow decrease (Fig. 5). With the electrodes sintered at atmospheric pressure and those sintered at 0·28 MPa, the yields did not fall below 80% over the whole time of operation (2 200 and 4 250 h, respectively). The perhydroxyl ion concentration in the solution, which also has an influence on the current yield, varied from 0·7 to 1·7 mol dm^{-3}. With electrodes prepared using higher pressures, the decrease in the current yield occurred much more rapidly.

The decrease of the current yield with the time of polarization is determined, above all, by the increase in the wetted surface area of the electrode, since the latter gives rise to a greater rate of peroxide decomposition in comparison with the rate of oxygen reduction which is controlled primarily by the transfer of dissolved oxygen on to the internal surface of the electrode[10]. It is however difficult to account for the observed effect of the pressure applied in electrode sintering on the time dependence of current yield.

The results of our measurements have indicated that porous electrodes prepared by hot-pressing at pressures up to a few tenths of MPa are capable of producing relatively concentrated alkaline solutions of hydrogen peroxide at current yields of 80 to 90%, with lifetimes as long as several thousand hours.

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