

POROUS ELECTRODES FOR THE PREPARATION OF PEROXIDE BY REDUCTION OF OXYGEN; INFLUENCE OF THE CONTENT OF POLYETHYLENE

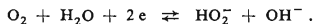
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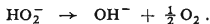
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With porous electrodes prepared by pressing a mixture of carbon black and polyethylene powder, the influence of the content of the binder on their electric resistance, wettability, current density, and current yield of peroxide during reduction of oxygen was studied.

Cathodic reduction of oxygen on electrodes from carbonaceous materials at potentials more positive than 0.5 V (against hydrogen electrode in the same solution) in alkaline medium leads to perhydroxyl ions as a relatively stable product^{1,2}:



It was found in the previous work³ that during reduction of oxygen on porous electrodes the current yield of peroxide depends mainly on the catalytic activity of the electrode material with respect to the decomposition of HO_2^- ions:



Since the characteristics of porous electrodes are much dependent on the content of the binder, we decided to study this effect in more detail. The studied electrodes, prepared from furnace black and polyethylene, differ from common semihydrophobic electrodes⁴, since both their components are typically hydrophobic. Therefore, we complemented our studies of the formation of peroxide by measurement of the quantity of electrolyte in the electrode pores.

EXPERIMENTAL

Preparation of electrode. A mixture of furnace black of 10 m²/g specific surface area and powdered polyethylene Hostalen of 80 μm mean particle size was spread into a nickel mesh and placed between two silicon rubber plates. Several such sandwich layers were placed in a metallic mould and tightened with screws in a defined manner. The mould was heated in an oven to 175°C for 15 min. Owing to a large thermal expansion of the silicon rubber, the mixture was during heating subjected to a large pressure which was distributed evenly over the entire electrode surface⁵ with respect to the elasticity of the rubber. The electrodes prepared in this way were discs of 31 mm diameter, about 0.8 mm thickness, and they contained 50–60 mg of the material per cm².

Measurement. The electric resistance of the electrodes was measured by the four-electrode method on samples of dimensions $29 \times 8 \times 1$ mm, prepared analogously as the electrodes, but containing no nickel mesh. The voltage between the probes was measured by a digital voltmeter of the type NR 50 (Metra, Blansko).

The apparent density of the electrodes was calculated from the dimensions and mass of the mentioned samples.

The content of electrolyte in the electrode was determined as follows. The electrodes were weighed in the dry state, inserted into the electrolyser and polarized at constant potential, while they were optionally fed with oxygen. The electrodes were taken out at intervals from the electrolyte, dried with filter paper and weighed. Their porous structure was determined by mercury porosimetry.

The polarization curves of the electrodes and current yields were measured as in the preceding work³. Potentials were measured against Hg/HgO electrode in 5M-KOH at 20°C.

RESULTS

Fig. 1 shows the influence of the content of polyethylene (PE) on the density of the porous electrode and its electric resistance. The density of the mixture increases with the PE content up to 40% PE while its resistivity decreases. At higher contents of PE the density of the mixture does not change any more but its resistivity increases.

The wettability of the electrodes expressed by the quantity of electrolyte referred to unit volume of the porous mixture is maximum for the electrodes containing 20–30% PE and decreases monotonously with further increasing content of PE (Fig. 2). The fraction of drowned pores is very low for all electrodes under study:

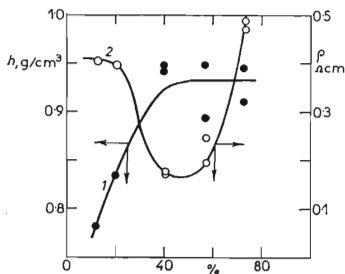


FIG. 1
Influence of PE Content in Porous Electrode (wt.%) on its Density (1) and Resistivity (2)

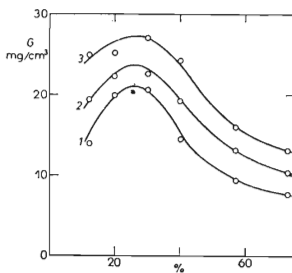


FIG. 2
Influence of PE Content in Porous Electrode on Degree of Drowning
Electrode soaked after 1 20 h; 2 66 h; 3 470 h. The samples were completely dipped in the electrolyte.

after 66 h when the samples were dipped in the electrolyte, their pores were drowned only to 2–4%.

The electrodes become more wetted during cathodic polarization, when the reduction of oxygen proceeds (Fig. 3). It is seen from the curves that the rate of wetting of the pores is the higher the more negative is the polarization. The wetting of the pores is irreversible as evidenced by the constant quantity of the electrolyte after changing the electrode potential from -0.8 to -0.5 V (curve 1c). If the electrodes were washed, dried and again polarized, they were wetted more rapidly than after the first wetting (compare curves 1d,a).

It follows from analogous time dependences of the current and quantity of the pore electrolyte that the rate of oxygen reduction on the studied electrodes increases with the degree of drowning. This current increase is slow, making the polarization curves less reproducible.

Fig. 4 shows the polarization curves of oxygen reduction on electrodes containing 12–73% PE. The influence of the potential and duration of previous polarization of the electrodes on the current density is here manifested by much larger currents measured during backward polarization.

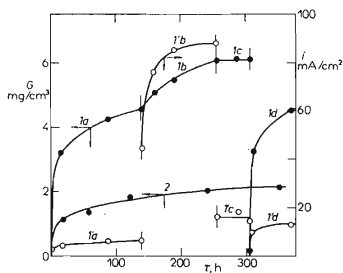


FIG. 3

Degree of Drowning (1a–d) and Current Density of Oxygen Reduction (1'a–1'd) as Functions of Duration of Polarization of Porous Electrode

Polarization -0.5 V (1a, 1'a, 1c, 1'c, 1d, 1'd); -0.8 V (1b, 1'b). Curve 2 was measured in currentless state, the potential was about -0.1 V. The electrode was fed with oxygen at 2.67 kPa overpressure (20 mm Hg), the other side was in contact with 5M-KOH.

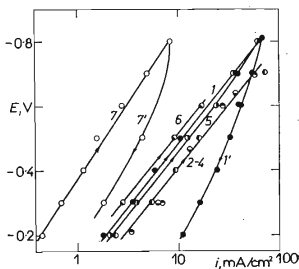


FIG. 4

Polarization Curves of Oxygen Reduction on Electrodes with Different PE Content

Content of PE in wt. %: 1,1' 12 ●; 2,20 ○; 3,30 ○; 4,40 ○; 5,47 ○; 6,57 ○; 7,7' 73 ○. Arrow denote direction of measurement of the potentials.

The dependences of current yields of the peroxide on the electrode potential are illustrated in Fig. 5. With an electrode containing 12% PE, a marked influence of the duration of polarization on the current yield of the peroxide was found (compare curves 1 and 1'). At higher contents of PE, this influence was not distinguishable.

DISCUSSION

The lowest resistivity was measured with dry electrodes containing 40% PE. The drop of the resistivity in the region from 15 to 40% PE can be attributed to binding properties of PE counteracting the elasticity of the carbon black, whereby a more compact body with a better contact among the particles is formed. In accord with this, an increase of the apparent density of the electrode mass with PE content in the mentioned region was observed. The resistivity of the mixtures increased with PE content above 40%, apparently as a result of increasing fraction of the nonconducting binder. However, the resistivity of all mixtures was so small that the voltage drop in the solid phase during operation of the electrodes was negligible (at most 1–2 mV) and could not cause an unequal current distribution.

Structure of the electrodes. The carbon black used in the preparation of the electrodes contained particles of a spherical shape of a mean diameter of 0.1–0.2 μm (ref.⁶). These were bonded in aggregates of a chain-like structure, which were after milling the black several tens μm in length. The particles of PE were also rather large, most particles were 50–100 μm in size (measured microscopically). Mercury porosimetry, detecting pore radii in the range 0.075–5 μm , revealed that the electrodes contained prevalingly pores with radii of the order of 0.1 μm . Their content was roughly directly proportional to the content of the furnace black in the electrode, hence it is apparent that these are intergranular pores. The electrodes did not contain pores smaller than the detection limit of the method used, as evidenced by the low BET surface area (9.8 ml/g). Hence, the particles of the furnace black are nonporous in accord with the literature⁶. The electrodes,

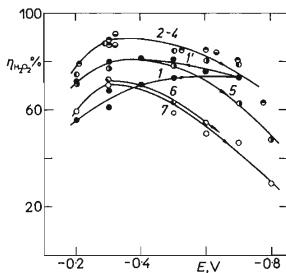


FIG. 5
Dependences of Current Yield of Peroxide
on Potential

The meaning of symbols as in Fig. 4.

however, contained also pores larger than $5\ \mu\text{m}$; their content was determined by the difference between the total porosity calculated from the apparent density of the electrode and the porosity determined by mercury porosimetry. Thus, electrodes with 12% PE contained $0.2\text{--}0.3\ \text{cm}^3/\text{g}$ of these larger pores, while those with 40% PE only $0.02\text{--}0.08\ \text{cm}^3/\text{g}$. Larger pores in electrodes with 12% PE were obviously formed by expansion of the mixture after pressing due to elasticity of the carbon black. Electrodes with a higher PE content are more rigid, the expansion being hindered by the binder.

The above results help to elucidate the influence of the content of PE in the electrode on its wetting properties in the currentless state (Fig. 2). The drop in the quantity of the pore electrolyte with increasing content of PE above 30% can be attributed to the fact that the electrolyte is bound in the pores formed by the particles of the carbon black. The low electrolyte content in electrodes with 12% PE is apparently caused by a large content of wide pores which are difficultly filled with electrolyte, preventing its penetration into the body of the electrode.

The increase in the wettability of the electrodes during their cathodic polarization is partly due to a decrease in the wetting angle when the potential becomes more negative than the zero charge potential⁷, which is for carbon equal to $-0.07\ \text{V}$ against normal hydrogen electrode⁸ ($-0.1\ \text{V}$ against Hg/HgO in 5M-KOH). Another reason for the increasing wettability was considered by Hull and James⁹: during reduction of oxygen or evolution of hydrogen in alkaline electrolytes OH^- ions are formed at the three-phase boundary in the electrolyte film in a concentration much higher than in the bulk of the electrolyte. This is compensated by water moving toward the three-phase boundary and as a result, the electrolyte creeps along the pore surface.

The low wettability of all the studied mixtures is due mainly to a low content of surface oxygen groups in the carbon black⁶, which leads to a low heat of wetting in water^{10,11}. During cathodic reduction of oxygen, however, the carbon black undergoes surface oxidation, whereby its hydrophilicity increases. Therefore, during polarization of a previously polarized electrode, which was washed and dried, the wetting proceeds more rapidly than for the first time (curve 1*d*, Fig. 3).

It follows by analogy between the curves of current density and those of electrolyte content (Fig. 3) that the current density increases with the degree of drowning of the electrodes under study. Also, it is seen by comparison of the polarization curves of oxygen reduction on electrodes with different content of PE (Fig. 4) that the current density is in the whole studied region the smaller the less wettable is the electrode (Fig. 2). For the same reason, during measurement of the reverse polarization curves (curves 1' and 7', Fig. 4) the current is much higher than normal (curves 1 and 7). The wetted surface area has obviously a decisive influence on the current density.

The polarization curves measured in the direction of decreasing potential are approximately linear with a slope of $0.37\text{--}0.47\ \text{V}$, which however is not simply

related to the kinetics of the electrode process since the slope was influenced by the wetted surface area changing during the measurement.

As follows from Fig. 5, the content of PE in the electrode has an influence also on the current yield of the peroxide, which was highest on electrodes containing 20–40% PE, *i.e.*, on electrodes which were relatively easily wetted. This can be explained as follows. In such well wetted electrodes the transport of HO_2^- ions from the pores into the bulk of the electrolyte is less hindered, their concentration gradient is smaller and their decomposition in the pores is slower¹². In accord with this explanation, *e.g.*, with an electrode containing 12% PE an increase of the current yield of the peroxide with the duration of polarization was observed (curves 1 and 1', Fig. 5).

The increase of the current yield of the peroxide with decreasing potential or with rising current density in the potential region of the two-electron reduction of oxygen (above -0.4 V) is in accord with the dependence calculated from the transport equations for oxygen and HO_2^- ions in the electrode pores¹². The drop in the current yield of the peroxide at potentials more negative than -0.4 V is due to HO_2^- ions being partly reduced².

It can be concluded that electrodes prepared from carbon black and powdered polyethylene have good mechanical properties and are resistant against drowning, which is the usual cause of a short life time of this sort of electrodes. On the other hand, they can be loaded with smaller currents than electrodes containing a teflon binder^{13,14}. Their disadvantage is also in low initial currents, which increase during their polarization as the wetting of their surface proceeds.

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