STUDY OF THE REDUCTION OF OXYGEN
ON A CARBON PASTE ELECTRODE IN AN ALKALINE MEDIUM

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The reduction of oxygen was investigated by voltammetry on a rotating disc electrode made from carbon paste. Oxygen was reduced irreversibly *via* hydrogen peroxide as an intermediary product yielding two unequally high waves. A small part of the hydrogen peroxide formed was reduced during the first step already thus contributing to a small extent to the formation of the first oxygen wave. As was evident from the fact that at higher revolution rates both waves fall below the theoretical value of a two electron process, the paste electrode was not active over its entire surface. Haemin present in the solution and in the paste acted as catalyst for the reduction of both hydrogen peroxide and oxygen.

A paste electrode[1,2] is prepared by bonding and filling the voids of powdered graphite with paraffin oil or another suitable water insoluble material. The electrode is easy to prepare, and was used for studying a number of redox systems[3-9]. Silicon-rubber-based graphite employed by Pungor and coworkers[10] proved useful even for preparing electrodes for continual analyses.

By measuring the overvoltage of oxygen reduction, voltammetric waves obtained on a stationary paste electrode[11] served to evaluate the electrochemical activity of carbon prepared to be used in fuel cells[12]. The present paper deals with investigating the reduction of oxygen on a carbon paste rotating disc electrode.

EXPERIMENTAL

The experimental technique employed was similar to that used previously when investigating the reduction of oxygen on a glassy-carbon rotating electrode[13]. Voltammetric curves are corrected by residual current values; the polarization sense from positive to negative potential values is indicated by (+ −), the reverse sense by (− +). In the figures, the polarization sense is indicated by arrows. Potentials are referred to a Hg/HgO reference electrode in 1M-KOH. Solutions were prepared from analytical grade purity chemicals and redistilled water. Hydrogen peroxide was free of stabilizers. If necessary, oxygen was expelled from the solutions with argon. Paste electrodes were prepared chiefly from spectral graphite powder of below 60 μm grain size. In some cases, various species of active carbon were used, some of them enriched with catalysts (see ref.[12]). Paraffin oil of spectral purity corresponding to Nujol (Merck, Darmstadt), toluene, benzene, tetrachloromethane (all analytical grade purity), and paraffin were used as binding agents. The working electrode was represented by a disc shaped (⌀ 3 mm) surface of the paste pressed into

a Teflon cylinder mounted on a rotating axis. Reynolds criteria were calculated for 64 and 6000 r.p.m. (15·1 and 1414, respectively); Nernst diffusion layers for the reduction of oxygen in 0·1M-KOH for the limiting revolution rates were also calculated ($7·9 . 10^{-3}$ and $8·1 . 10^{-4}$ cm, respectively).

RESULTS

Reduction of Oxygen and Reduction and Oxidation of Hydrogen Peroxide

The nature of the residual current on the paste carbon electrode is similar to that described in the study on glassy-carbon electrodes[13]. In paste electrodes, its magnitude depends mainly on the type of the binding agent. Electrodes bonded with benzene yielded high values whereas low values were found in those bonded with paraffin. No dependence was found on the convection rate of electrolyte. On a paste electrode prepared from spectral graphite bonded with paraffin in 0·1M-KOH, oxygen is evolved at +0·75 V, on one bonded with paraffin oil at +0·65 V (vs Hg/HgO). Hydrogen evolution begins at −1·2 V.

On the above described oxygen electrode, oxygen is reduced in two irreversible waves (Fig. 1). The lowest oxygen overvoltage value was found in the case of an electrode bonded with benzene; the results, however, were poorly reproducible due to the high evaporation rate of benzene. On electrodes containing paraffin, the overvoltage values were very high and increased with the paraffin concentration in the paste. The value of the half-wave potential found with an electrode bonded with paraffin oil was −0·242 V at 512 r.p.m. and $(+ -)$ polarization. As the rotation speed increased the half-wave potential was shifted to more negative values. The value of the αn parameter

$$\alpha n = (RT/F) \, d\ln \left[(i_1 - i)/i \right] \, dE$$
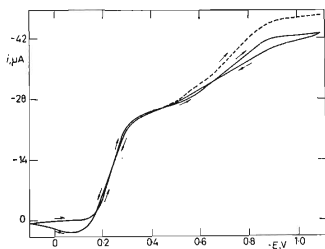

Fig. 1

Reduction of Oxygen on Carbon Paste Electrode Bonded with Paraffin Oil (35% by weight)

Curve obtained after adding $1 . 10^{-8}$ mol/ml of Fe^{3+} salt to 0·1M-KOH solution is dashed. 512 r.p.m., 400 mV/min.

was calculated from the plot of oxygen reduction to hydrogen peroxide and amounts approximately to 0·7 for an electrode bonded with paraffin oil and 0·5 for one bonded with paraffin. When using a paste electrode, a pre-wave to the second wave of the reduction of oxygen often appears in a 0·1M-KOH solution; this prewave slightly increases as the concentration of iron in the solution raises; at the same time a slight increase of the second wave of oxygen reduction is observed.

A paste electrode bonded with benzene yielded high peaks of oxygen reduction during $(+ \ -)$ polarization especially in the case of the first polarization curve (Fig. 2), evidently at the expense of oxygen present in the paste (oxygen is almost six times as soluble in benzene as in water). For the first wave of oxygen reduction the experimental current values obtained on an electrode bonded with paraffin oil are somewhat higher than theory, and fall below theory of a two-electron process at higher revolution rates (Fig. 3). When using paraffin as binding agent, values lower by approximately 25% were observed than in the case of a paste bonded with paraffin oil. The sum of both reduction waves obtained on either of these electrode types was about 30% lower than that corresponding to a four-electron reduction. The dependence of the first reduction wave equally as the sum of both the waves on the root of the rotation speed of the electrode is not in strict agreement with Levič equation (Fig. 3); especially at higher rates it falls below the theoretical straight line.

The paste electrode bonded with paraffin oil polarized $(- \ +)$ in an alkaline medium containing oxygen yields an anodic peak which is assumed to belong to oxidation of a superoxide anion-radical HO_2^- appearing as an intermediary of oxygen reduction. More detailed information on the subject is given elsewhere[14].

Reduction of hydrogen peroxide in 0·1M-KOH proceeds, in the absence of oxygen,
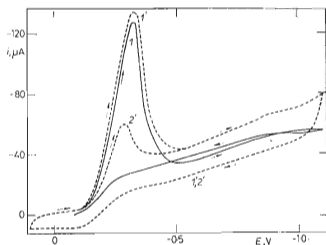

Fig. 2

Reduction of Oxygen on Carbon Paste Electrode Bonded with Benzene

Dashed curves include residual currents. Curve 2' was recorded immediately following curve 1'. 512 r.p.m., 400 mV/min.

irreversibly at potentials corresponding to the second wave of oxygen reduction (Fig. 4). Hydrogen peroxide is oxidized at very positive potentials. When using a stationary electrode, the oxidation wave is clearly visible, when using a rotating electrode, the wave merges with the oxygen evolution current. The height of the wave of hydrogen peroxide reduction is considerably lower than that corresponding to a two-electron reduction and its dependence on the root of the revolution rate markedly deviates from the theoretical Levič straight line to lower values.

Influence of Haemin

The paste electrode is highly sensitive to haemin in the solution. In 0.1M-KOH containing oxygen a pre-wave to the second oxygen (so called peroxide) wave appears at minute concentrations already (Fig. 5). As the concentration of haemin increases the pre-wave increases at the expense of the peroxide wave. At concentrations above 10^{-7}M, the peroxide wave is shifted to more positive potentials and in some cases even surpasses its original height to reach the theoretical value of a two-electron process. In such a limiting case (e.g. after an addition of 10^{-6}M of haemin into the
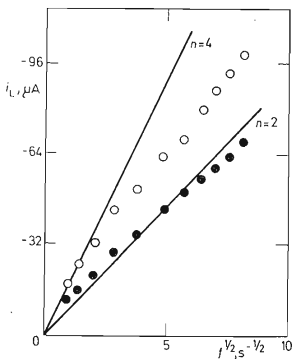
Fig. 3

Limiting Currents of ● First Wave and ○ Sum of Both Waves of Reduction of Oxygen vs Root of Rotation Speed of Carbon Paste Electrode Bonded with Paraffin Oil

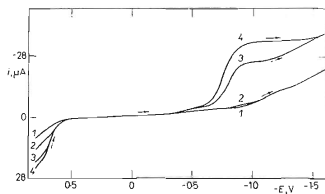Straight lines correspond to theoretical values for 2- and 4-electron processes.

Fig. 4

Reduction and Oxidation of Hydrogen Peroxide ($5 . 10^{-4}\text{M}$) in 0.1M-KOH (1)

2, 3, 4 after addition of haemin at concentrations 10^{-11}, 10^{-10}, and 10^{-9} mol/ml. Carbon paste electrode bonded with paraffin oil, 1050 r.p.m., 500 mV/min.

solution) the sum of both oxygen waves is directly proportional to the root of the revolution rate of the electrode. During long term measurements, the concentration of haemin in the solution falls due to its adsorption on the vessel walls and the Teflon holder of the electrode; the haemin pre-wave decreases unless there was a sufficient quantity of haemin in the solution. A similar effect of haemin was observed with a solution of hydrogen peroxide free of oxygen (Fig. 4). At haemin concentrations of 10^{-7}M, hydrogen peroxide ($5 . 10^{-4}$M) is reduced in one wave only; the wave, however, is much larger and appears at more positive potentials than in the absence of haemin. At concentrations of 10^{-6}M, the height of the reduction wave of hydrogen peroxide catalysed with haemin reaches almost the theoretical value of a two-electron process; at higher concentrations, however, a visible decomposition of hydrogen peroxide in the solution sets in, especially in solutions which were left standing for longer periods of time. Haemin also induces an increase in the oxidation wave of hydrogen peroxide. In a 0·05M borax solution, the difference in the half-wave potential of both oxygen waves is considerably smaller than that in 0·1M-KOH. An addition of haemin results in an increase of the first wave of oxygen reduction. At 10^{-6}M haemin concentration one wave of oxygen reduction is observed. A similar influence of haemin consisting in a shift to more positive potentials was observed in the case of reducing hydrogen peroxide in solutions free of oxygen. After adding haemin to an acetate buffer solution, the same effect as that in borax occurs, only
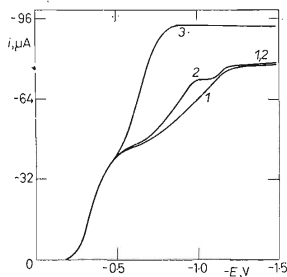

Fig. 5

Reduction of Oxygen on Carbon Paste Electrode

1 in 0·1M-KOH; *2* after adding 10^{-11} mol/ml and *3* 10^{-9} mol/ml haemin.
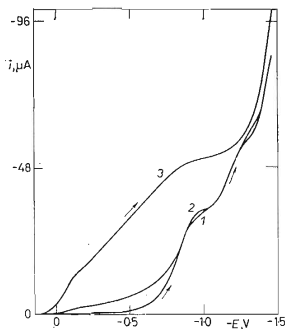

Fig. 6

Reduction of Oxygen in 1M Acetate Buffer pH 4·6 on Carbon Paste Electrode (*1*)

2 and *3* after adding 10^{-11} and 10^{-9} mol/ml haemin.

a part of the first wave of oxygen reduction is also shifted (Fig. 6). With pastes containing 10% by weight of haemin, oxygen reduction proceeds in a way similar to that taking place in solutions of higher haemin concentrations. An electrode with only haemin present in the paste gives very well defined anodic and cathodic peaks, not fully reversible.

DISCUSSION

The overvoltage of the reduction of oxygen to hydrogen peroxide is dependent to a large extent on the binding agent of the paste, increasing with its concentration. The overvoltage decreases markedly if a part of the spectral graphite in the paste is replaced with active carbon. Compared to a glassy-carbon electrode or to electrodes of solid graphite, the electrode kinetics parameters of oxygen reduction are much more dependent on the mode of preparation of the electrode. The results obtained on a paste electrode bonded with 15% by weight of paraffin were close to those obtained on a glassy-carbon electrode[13]. The charge transfer coefficient was $\alpha = 0.5$ and the rate constant of the electrode reaction at a standard potential of the system oxygen-hydrogen peroxide $k^0 \sim 5 \cdot 10^{-5}$ cm s^{-1}. The rate of the overall reaction of oxygen reduction is determined, similarly as on electrodes made from other materials, by the acceptance of the first electron forming the superoxide anion, whose existence is supported by the anodic peak observed at voltammetric curves during $(- +)$ polarization[14]. The electrode kinetics parameters obtained with a paste electrode bonded with paraffin oil are less reproducible, α was $0.6-0.7$ and k^0 was of the order of 10^{-4} cm s^{-1}.

The decrease of the first wave of oxygen reduction and especially of the sum of both waves below the theoretical value which was observed at higher revolution rates may be explained similarly as that observed in the case of glassy-carbon electrode[13], namely by the existence of inactive sites on the electrode surface. The experimental conditions do not permit calculation of the radii of the active and inactive sites of the electrode surface by Landsberg procedure[15,16]; it is, however, possible to estimate the size of the inactive sites from the dependence of the magnitude of the limiting current of oxygen reduction on the root of the rotation rate (Fig. 3). In the case of the limiting current, a region of a practically zero concentration of the electro-active species given by Levič equation is formed at the entire surface of the electrode so far as, at low revolution rates, the Nernst diffusion layer is sufficient in comparison with the dimensions of the active sites. At higher revolution rates the thickness of the Nernst diffusion layer becomes comparable with the size of the inactive sites, and a zero concentration of the electroactive species near these centers can no longer be assumed. The diffusion of oxygen along the electrode from inactive to active sites is not sufficient to counterbalance the fact that no reduction proceeds on the inactive sites. At such revolution rates the magnitude of the limiting current falls

below the two-electron theoretical reduction value. At 4000 r.p.m. a clear decrease in the magnitude of the limiting current value below theory is observed; the Nernst diffusion layer in this case is 6·5 μm. Inactive sites would probably appear in the interstitial voids (graphite below 60 μm grain size) which are filled with a rather thick layer of paraffin oil (or another binding agent). The inactivity of the electrode surface is more pronounced in the reduction of hydrogen peroxide than in the reduction of oxygen. The oxygen molecule is non-polar and therefore partly soluble in the aprotic solvent whereas the polar HO_2^- anion is expelled from the medium.

Similarly as on a mercury dropping electrode[17], the peroxide pre-waves appearing during oxygen reduction especially in more concentrated solutions may be explained by the reduction of ferric ions present in trace quantites (10^{-9}M is sufficient), and their regeneration with hydrogen peroxide. A similar influence on the decrease of the overvoltage of peroxide reduction as is that of ferric ions has a porphyrine complex of iron in haemin. The influence of haemin decreases as the pH of the supporting electrolyte falls, probably due to its lower solubility. Due to the fact that the catalyst is adsorbed on the electrode surface, its effect on the reduction of hydrogen peroxide is stronger on a paste electrode than on a mercury dropping electrode. In an acetate buffer solution, haemin also brings about a decrease in the overvoltage of the reduction of oxygen -- a pre-wave to the first oxygen wave is observed. In this case, however, no regeneration of the ferric complex with hydrogen peroxide is possible. Most probably, oxygen reduction is facilitated by the formation of an adduct haemin-oxygen[18].

Determination of reaction kinetics of both the ferric ions regeneration with hydrogen peroxide and the haemin-oxygen adduct formation has not been possible; haemin adsorbs on the glass walls of the vessel and on the electrode, preventing thus accurate concentration measurements to be made in dependence on the catalytic effects. A further complicating factor is the fact that the first oxygen wave is always higher than the so called peroxide wave. A portion of the oxygen peroxide resulting through the reduction of oxygen seems to be reduced more easily, or possibly a decomposition on the active carbon surface proceeds with oxygen and water forming.

In the presence of haemin the limiting current of the peroxide wave increases and reaches the theory at higher revolution rates of the electrode. This phenomenon may be explained by the coverage of the inactive sites of the electrode with adsorbed haemin. Reduction of haemin on a paste carbon electrode proceeds, contrary to the reversible process taking place on a mercury dropping electrode, with an overvoltage falling with the decrease in pH. The oxygen overvoltage increasing towards lower values of pH, the catalytic influence of haemin in more acid solution results in an increase of the first wave of the reduction of oxygen.

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