

STUDY OF THE ELECTROCHEMICAL REDUCTION OF OXYGEN ON GLASSY CARBON IN AN ALKALINE MEDIUM

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Received March 20th, 1972

Voltammetric curves of the reduction of oxygen in an alkaline medium obtained on a glassy-carbon rotating disc electrode exhibited two reduction waves suggesting an irreversible reduction of oxygen proceeding *via* hydrogen peroxide as an intermediary product. The first wave reached or slightly exceeded the theoretical two-electron height value only after a definite pre-treatment of the electrode surface. The second (peroxide) wave was similar to that obtained by reducing hydrogen peroxide in the absence of oxygen, and its height was considerably lower than that corresponding to a two-electron process. Both the waves exhibited deviations from the Levich equation especially during high revolution rates of the electrodes. The deviations were strongly dependent on the history of the electrodes, and were probably due to the inhibition of oxygen or hydrogen peroxide reduction, taking place on certain sites of the electrode surface.

Vitreous carbon (glasslike carbon) which has originally been developed as a material stable at high temperatures in atomic reactors, has recently found application in a number of other fields, *e.g.* for preparing electrodes for electroanalytical purposes^{1,2}. The study of the reduction of oxygen on a stationary glassy-carbon electrode contributed not only to the knowledge of the irreversible nature of the process but also brought information regarding its application for determining oxygen³. The present paper is meant to help in elucidating some features in the electrode process. To this purpose, voltammetry on a rotating disc electrode was chosen as the tool, due to the fact that it simplified the mass transfer to the electrode. During our investigations⁴, a short communication appeared⁵ containing a comparison of the rate of the reduction of oxygen on electrodes of pyrographite and glasslike carbon. The paper, however, gives no further particulars regarding the latter.

EXPERIMENTAL

Two types of rotating disc electrodes were employed, both manufactured at our Institute. One was working over the range from 64 to 2048 r.p.m., permitting an accurate setting of the speed with the aid of gears, the other, belt driven, worked from 250 to 8000 r.p.m. the speed being continuously measured by a photoelectrical reader and counter system⁶. The test vessel was of a three compartment type⁷ to prevent the mixing of the reference electrode solution with the electrolyte. The electrical resistance of the vessel was below 400 Ω . Potentials were measured against a large surface Hg/HgO electrode in 1M-KOH to which all the values quoted are related.

The *i-E* curves were registered mostly with a Radelkis polarograph type OH-102 (Hungary) or a Radiometer type PO-4 (Denmark). The voltammetric curves were registered in a two-

electrode system; in the case of higher currents, corrections were introduced for the iR drop. If not stated otherwise, only reproducible curves were evaluated. The values measured are decreased by the residual current values. The symbols (+ -) and (- +) indicate the sense of the polarization. In the figures, the polarization sense is indicated by arrows.

The working electrode was of glassy-carbon GC-10, Tokai Electrode Mfg. Co. Tokyo, Japan⁸, and had the shape of a disc of 3 mm diameter inserted into a teflon cylinder. GC-10 has a minute porosity (0.2–0.4% by volume), a high purity, a low electrical resistance of the order of $10^{-3} \Omega \cdot \text{cm}^{-1}$, and a high mechanical strength. Its further structural properties will be quoted in the discussion of results.

The results were compared to those obtained on disc electrodes of silver and platinum of the same size, used previously for studying the reduction of oxygen^{7,9,10}. The surface of the glassy-carbon electrode was submitted to various types of mechanical finishing. The original surface of commercial samples is denoted by *A*, the lathe-turned surface by *B*, the emery 6/0 (SIA) ground surface by *C*, and the carborundum ground surface by *D*. The electrochemical finishings are denoted by the letter of the respective mechanical treatment and by a numerical subscript explained in the legend of the pictures or the table. After the mechanical treatment, the electrode was rinsed with a large quantity of redistilled water.

The solutions used were prepared from analytical grade chemicals and redistilled water, the hydrogen peroxide was free of stabilizers. Measurements were made in solutions saturated with air oxygen or in solution purged of oxygen by a stream of argon.

The following values of the Reynolds criterion were calculated: 15.1 and 1414 for 64 and 6000 r.p.m., respectively. The corresponding Nernst diffusion layers calculated for 0.1M-KOH and oxygen reduction were $7.9 \cdot 10^{-3}$ and $8.1 \cdot 10^{-4}$ cm, respectively.

RESULTS

Residual Current

The shape and magnitude of the residual current are strongly dependent upon the mechanical and electrochemical pre-treatments of the electrode. On a glassy-carbon electrode (Fig. 1) it has a similar nature as that obtained on silver⁷ or platinum^{9,10} in an alkaline medium. This analogy implies that the wave *A* corresponds to the reduction of surface oxides and the wave *B* to the destruction of the layer of surface adsorbed hydrogen atoms. After treatments differing from that given in Fig. 1, the residual current may be considerably lower. The waves of the reduction of oxides and the formation of the adsorbed atomic hydrogen are often ill-developed and

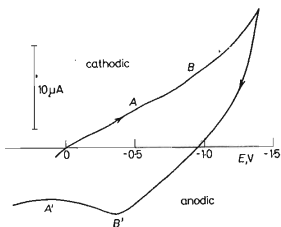


FIG. 1
Residual Current on a Glassy-Carbon GC-10
Electrode in 0.1M-KOH
Finish *D*, 500 mV/min.

merge into an extended low single wave. To make a comparison between the roughness of the electrode surface and the electrochemical properties of the oxygen reduction, the area bounded by the residual current curve and the potential axes at E_0 and $E - 1.0$ V was measured. *E.g.* after pre-treatment B , the coulombic efficiency of the area bounded by the residual current during polarization (+ -) and the axis in the potential interval 0-1.0 V, the value was $8.48 \cdot 10^{-3}$ C/cm² whereas in the case of treatment D $2.26 \cdot 10^{-2}$ C/cm² was found.

Electrochemical finishing, especially anodic pre-polarization at 0.2-0.5 mA in an acid medium, produced highly developed surfaces yielding the most favourable although badly reproducible conditions for the reduction of oxygen. During all experiments, the independence of the residual current on the rotation speed of the electrode was controlled.

Oxygen Reduction

In 0.1M-KOH, the reduction proceeds in two irreversible waves, the first wave being always higher than the second one (Fig. 2). The latter is mostly less well developed; especially on high area surfaces its limiting current is soon transformed into the current belonging to the evolution of hydrogen.

During polarization (- +) the half-wave potentials of the reduction of oxygen are more positive than during the reversed process, the difference amounting in some cases up to 20 mV. The half-wave potentials are more positive on electrodes with that type of mechanical or electrochemical pre-treatment which produces rougher surfaces. Electrochemical treatment of the electrodes, *e.g.* alternating polarization between the potential of the evolution of hydrogen and oxygen may reduce the overvoltage of oxygen reduction also as a consequence of purging the electrode of some adsorbed species which would otherwise inhibit the process. As may be expected for an irreversible reaction, the half-wave potentials of the oxygen reduction waves are shifted to more negative values as the number of revolutions of the electrode is increasing. After an electrochemical pre-treatment, the overvoltage of both the oxygen reduction and hydrogen evolution decreases more than after a mechanical treatment. Values obtained on a highly developed surface after treatment D_2 (Table I) were close to the reversible half-wave potential value $E_{1/2} - 0.09$ V obtained on a mercury dropping electrode in the same electrolyte.

TABLE I

Half-Wave Potentials Obtained on Electrodes with Various Surface Finishings

	Rotation speed (r.p.m.) and sense of polarization	Surface finish					
		B_1^a	B_2^a	B_3^a	B_4^b	D_1^c	D_2^c
512	(+ -)	-0.285	-0.273	-0.254	-0.253	-0.185	-0.166
	(- +)	-0.272	-0.263	-0.235	-0.243	-0.163	-0.130
256	(+ -)	-0.250	-0.249	-0.233	-0.247	-0.174	-0.150
	(- +)	-0.234	-0.243	-0.220	-0.238	-0.152	-0.113
128	(+ -)	-0.238	-0.233	-0.217	-0.228	-0.158	-0.141
	(- +)	-0.229	-0.222	-0.208	-0.219	-0.136	-0.108

^a Pre-polarization in 0.1M-KOH at +0.1 V and -1.4 V for 1 (B_1), 5 (B_2), and 15 (B_3) minutes;

^b 15 min only at +1.0 V; ^c anodic polarization at 200 μ A in 0.1N-H₂SO₄ for 2 (D_1) and 5 (D_2) min.

For a sufficiently irreversible process, the points obtained by the "logarithmical analysis" [$\log(i_L - i)/i = f(E)$] of the first wave of oxygen reduction lie on a straight line. If the overvoltage of the first reduction wave is low, e.g. treatment D_2 (Table I), the points of the logarithmical analysis lie on a curve whose shape corresponds to that of a quasireversible process^{11,12}. Aside from the half-wave potential values, the product ωi_k has also been read-off the logarithmical analyses. These values greatly depend on the surface area of the electrode and consequently also on its history. The values ωi_k were in the range of 0.5–0.6. The effect of treatments D and C on the residual current and the electrochemical reduction of oxygen was of the same character.

The values of the limiting current of the first wave of oxygen reduction are, with an increase in the number of revolutions, below the theoretical value (Fig. 3). The deviations are more apparent especially on electrodes with a less developed surface (e.g. with the original surface A and also with the surface B). The smallest deviations from the Levíč equation were found on electrodes with the surface C .

Electrodes with a well developed surface exhibited a drop in the limiting current during high revolution rates and the polarization (+ -) increasing (Fig. 2). This shape of the limiting current was, however, badly reproducible. It was mostly observed in those cases where the limiting current was attaining the value of a two-electron process or slightly above during low revolution numbers (Fig. 3). (The maximum value observed was 15% above theory.)

A more pronounced drop below the theory of the limiting current was obtained in a wave corresponding to the reduction of the hydrogen peroxide resulting on the electrode by the reduction of oxygen (Fig. 3). This drop is even more dependent on the history of the electrode than in the preceding case. At potentials close to the foot of the irreversible wave of oxygen reduction,

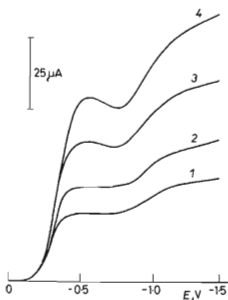


FIG. 2

Oxygen Reduction Polarization Curves on Glassy-Carbon GC-10 Electrodes in 0.1M-KOH after Correction by the Residual Current

Polarization sense (+ -), 500 mV/min, finish C. Rotation speed (r.p.m.): 1 425, 2 890, 3 2185, 4 4080.

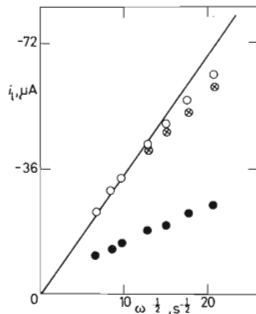


FIG. 3

Limiting Currents of the Oxygen Reduction Waves vs Rotation Speed of Glassy-Carbon GC-10 Electrode in 0.1M-KOH

○ i_{1max} , ⊗ i_{1min} of the first oxygen reduction wave, ● i_1 of the second oxygen reduction wave. Polarization sense (+ -), finish C.

the current value is independent of the rotation speed (Fig. 4), *i.e.* of the magnitude of the mass flow to the electrode.

Reduction and Oxidation of Hydrogen Peroxide

Irrespective of the history of the glassy-carbon electrode, the reduction of hydrogen peroxide is fully irreversible and proceeds at potentials corresponding to the second wave of oxygen reduction (Fig. 5). The height of the wave is considerably lower than that corresponding to the theory for a two-electron process; its dependence on the revolution speed is well below the linear dependence of the Levich equation. The deviations greatly depend on the pre-treatment of the electrode surface similarly as in the case of the second wave of the reduction of oxygen in the absence of free hydrogen peroxide. Fig. 5 depicts a wave obtained on an electrode pre-treated by the process *C* followed by an electrochemical activation. The peroxide wave is more than twice below the theoretical value. Inactive electrodes, *i.e.* mostly those with an undeveloped surface, exhibit only very low peroxide waves. Logarithmic analyses of the curves are linear, of a fully irreversible nature, the αn_k parameter being 0.3–0.4. The half-wave potential of the reduction of hydrogen peroxide shifts to negative values as the number of revolutions increases.

The anodic wave of the oxidation of hydrogen peroxide is placed 1 V more positively than the cathodic wave of its reduction and is also lower than that for a two-electron process. Its dependence on the revolution speed of the electrode also deviates from theory.

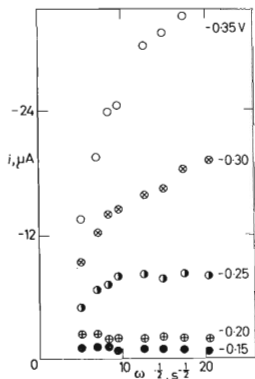


FIG. 4

Current of the First Oxygen Reduction Wave *vs.* Rotation Speed of the Electrode at Various Potentials for Glassy-Carbon GC-10 in 0.1M-KOH

Polarization sense (+ -), finish *C*.

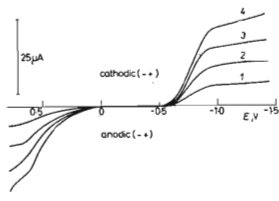


FIG. 5

Polarization Curves of Oxidation and Reduction of Hydrogen Peroxide in the Absence of Oxygen on Electrodes of Glassy-Carbon GC-10 in 0.1M-KOH

Finish *C* followed by electrochemical activation, 128 r.p.m., H_2O_2 conc.: 1 $0.635 \cdot 10^{-3} N$; 2 $1.27 \cdot 10^{-3} N$; 3 $1.905 \cdot 10^{-3} N$; 4 $2.54 \cdot 10^{-3} N$.

DISCUSSION

The history of the glassy-carbon electrode exerts a great influence on the height of the voltammetric waves of oxygen and hydrogen peroxide reduction. At high revolution rates and at low rates combined with smooth surfaces, the magnitude of the limiting current of the first wave of oxygen reduction is far below the theoretical two-electron value. For the reduction of hydrogen peroxide this drop is even greater.

The explanation may be associated with the structure of the glassy-carbon⁸, passing continuously from the amorphous *via* the turbostratic to the purely graphitic form. The macrostructure of glassy-carbon is isotropic, consisting of randomly oriented graphitic crystallites of 50 Å mixed with amorphous carbon, with a bonding similar to that in diamonds. As the temperature of the preparation process of glassy-carbon *i.e.* the pyrolysis of phenol-formaldehyde resins increases, the ratio of the graphitic structure raises. The material employed for our investigations contained about 75% by volume of the graphitic form. This composition suggests that the individual components will probably not possess equal electrochemical activities.

On a glassy-carbon electrode the residual current is larger than that obtained on smooth platinum and depends to a great extent on the history of the electrode. The waves belonging to the formation of surface oxides and to the adsorbed atomic hydrogen as well as their reduction or desorption of hydrogen are ill-developed so that they cannot serve for determining the true surface area of the electrode. The so called double layer region, so typical for a platinum electrode, when the electrode is free of the above cited layers is not obtained when working with glassy-carbon. Some information on the nature of the surface oxides which should be responsible for the waves observed might, however, be obtained from the analogy with the oxides formed through the reaction of gaseous oxygen with the surface of active carbon. Varying with the conditions of formation, a whole series of these surface compounds may be found¹³. The extended shape of the wave of formation or reduction of oxides on a glassy-carbon electrode may be due to the formation or reduction of two or more oxide species.

The fact that the value of the limiting current of oxygen reduction is below that given by the Levíč equation may be explained by the existence of sites which are generally electrochemically inactive or which are selectively inactive for the reduction of oxygen. These could possibly be the planes of the graphitic crystallites facing the solution with their aromatic π -orbitals ("cleavage surface"). A similar electrochemical electrode inactivity during the reduction of oxygen was reported by Morcos and Yeager¹⁴ who worked with pyrolytic graphite prepared at high temperatures and pressures. They postulate that oxygen cannot be adsorbed on a cleavage surface and that its reduction is thus retarded¹⁵. The planes with a bonding similar to that of diamond might be electrochemically totally inactive.

As has already been reported, the reduction of hydrogen peroxide on silver⁷ and platinum^{9,10} which on active electrodes starts at potentials slightly more positive

than the reduction of oxygen, is greatly influenced by surface processes. Hydrogen peroxide may be reduced through a reaction with the surface oxides or the hydrogen atoms adsorbed. In potential regions where there are no surface layers on the electrode, electrodes of silver or platinum exhibit a drop in the limiting current of hydrogen peroxide reduction or the four-electron oxygen reduction. Although glassy-carbon electrodes do exhibit some (ill-defined) reduction waves of both the surface oxide reduction and the hydrogen layer formation, the oxides are evidently of a completely different nature than those on silver or platinum. On more active electrodes where the oxide waves are higher and better developed, the oxygen wave approaches or even exceeds the theoretical two-electron reduction value. In these cases, a drop in its limiting current is observed at potentials when surface oxides would already be reduced.

A decomposition of hydrogen peroxide formed through reduction of oxygen on a glassy-carbon electrode will take place only to a small extent and only on highly active electrodes. This is in accordance with the high hydrogen peroxide oxidation overvoltage as well as the low value of the limiting current (below theory). Sabirov and Tarasevič⁵ observed no decomposition of hydrogen peroxide on the platinum ring of a vitreous carbon disc electrode on which oxygen was reduced. Hydrogen peroxide decomposition (10^{-3}M) has, however, been observed in a 0.1M-KOH solution agitated with a large area glassy-carbon disc, especially after prolonged contact¹⁶.

At higher concentrations of hydrogen peroxide ($>10^{-3}\text{M}$) in solutions freed of oxygen, a low wave corresponding to the reduction of oxygen formed by the decomposition of hydrogen peroxide was observed on highly active electrodes; we are, however, of the opinion that the difference between the heights of the waves of oxygen and hydrogen peroxide reductions are not substantially due to the decomposition of the resulting hydrogen peroxide. It is probable that the inactivity of the electrode surface influences the reduction of hydrogen peroxide more strongly than that of oxygen. The decomposition of hydrogen peroxide to oxygen and the reduction of hydrogen peroxide by surface oxides will influence the difference between the heights of the waves of oxygen reduction and hydrogen peroxide reduction to a slight extent only.

The surface of active electrodes is more developed and the surface area is therefore larger. The probability that the species hitting an electrode with an electrochemically unhomogeneous surface finds a suitable active site, is thus higher. It is however necessary that the Nernst layer, *i.e.* the layer in the proximity of the electrode, whose concentration gradient of the electrochemically active species controls the magnitude of the current, be sufficient in comparison with the distance between the active and inactive sites on the electrode surface. The smaller the thickness of the Nernst layer, the stronger will be the influence of the diffusion from the inactive to the active site along the electrode; the current will no longer be controlled by convection (following the Levič equation) only. This is also the reason why there

are larger deviations in the limiting currents of both the oxygen and hydrogen peroxide reduction from the theoretical values at high rotation speeds. The kinetic nature of the current, whose magnitude may be determined by the rate of the electrode process, *e.g.* the take-up of the first electron by the adsorbed oxygen molecule instead of the velocity of the mass transfer to the electrode, makes the height of the wave of the oxygen reduction current at potentials of its foot independent of the rotation speed.

The kinetic electrode parameters for the reduction of oxygen and hydrogen peroxide tested are related to the given pre-treatment of the electrode. In addition to coefficient αn_k which was close to 0.5, the electrode reaction rate constant was also calculated from the equation for an irreversible half-wave potential

$$(E_{1/2})_{\text{irr}} = (E_{1/2})_{\text{rev}} - (RT/\alpha n_k F) \ln (n F k^0 / \kappa_{\text{ox}}),$$

where $\kappa_{\text{ox}} = i_{\text{lim}}/C_{\text{ox}}$, and with the aid of the so-called kinetic currents in which no mass transfer takes place¹⁷. The kinetic currents were obtained by extrapolating the dependence $1/i - 1/\omega^{1/2}$ to the infinite value of the rotation speed. Several factors, *e.g.* the activity coefficients, the influence of the outer Helmholtz layer ϕ_2 , and some side reactions taking place on the electrode surface were neglected. For illustration, the value of the constant of the standard potential of the oxygen reduction k^0 obtained on the surface *C* was of the order of 10^{-4} cms^{-1} .

The low porosity and the chemical stability of glassy-carbon make it a suitable material for electroanalytical purposes. Allowance should, however, be made for its unhomogeneous structure. For this reason, the effect of the history of the electrode on the electrode process studied has to be thoroughly verified. A comparison with a standard is advisable not only after every change in the pre-treatment but also during measurements made after treatments of the same type. According to our experience, one of the best treatments tested is the finish *C*, *i.e.* grinding the electrode with a fine grain emery paper.

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Translated by M. Svata.