

Review Paper

Cathodic oxygen reduction on noble metal and carbon electrodes

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Received 7 February, 1994; accepted 24 May 1994

Abstract

Because of their high electrocatalytic activity and stability noble metals were thoroughly investigated for the cathodic oxygen reduction. Emphasis has also been placed on the study of oxygen reduction on carbon electrodes in alkaline media due to their relative stability, easy modification of surface properties, large availability and low price. The observed behaviour of oxygen reduction on noble metal and carbon electrocatalysts is surveyed here. The common mechanisms under Langmuir conditions of adsorption are also examined in an attempt to account for the reaction kinetics of oxygen reduction on metal-doped polymer carbons in alkaline solutions.

Keywords Electrodes, Noble metal; Carbon; Cathodic oxygen reduction; Oxygen

1. Introduction

The four-electron reduction of oxygen in either acid or alkaline solution is of primary concern due to its possible utilization in fuel cells and metal/air batteries on the basis of its high theoretical equilibrium potential of 1.229 V versus a hydrogen electrode in the same solution. The majority of research on this reaction has centred on the use of noble metal electrodes, due to their relative stability in acidic or alkaline solutions. Numerous studies to determine the mechanism of oxygen reduction on these noble metal electrodes have been conducted by Damjanovic and co-workers [1–18], Bockris and co-workers [19–21], Hoare [22–34] and many other investigators [35–112]. Through the use of the rotating ring-disc electrode the role of peroxide intermediates in these mechanisms has been studied by Damjanovic et al. [3,4,113], Genshaw et al. [114,115], and others, while additional studies on the importance of peroxide intermediates used stationary electrodes [116–119].

The research indicated that the kinetics of oxygen reduction were highly dependent on the specific electrode. To better define the influence of the electrode on oxygen reduction, research on noble metal alloy electrodes was conducted by several workers, namely Damjanovic et al. [120,121], Hoare [122], and Gnanamuthu and Petrocelli [123]. This influence of the

electrode on the kinetics of an electrochemically reaction is the primary concern in the study of electrocatalysis as defined in several comprehensive reviews and books [124–136].

Emphasis has also been placed on the study of oxygen reduction on carbon electrodes [137–140] due to their relative stability in acidic or alkaline solutions. Early studies by Berl [141] and Yeager et al. [142] of oxygen reduction on a variety of carbon electrodes indicated that in this case the oxygen was reduced to peroxide anions by a two electron process. Subsequent research by Taylor and Humffray [143,144] using glassy carbon electrodes and Appel and Appleby [145] using active carbon in the form of thin-film electrodes verified that oxygen reduction on carbon was principally a two-electron process to peroxide anions whose further dissociation necessary for the four-electron reduction could not be sustained by the carbon sites.

Further research dealt with developing carbon electrodes containing catalysts to aid in the decomposition of the peroxide intermediates to yield the four-electron reduction process. The major effort centred on the use of noble metals distributed on porous carbon electrodes, though only a small amount of data has been published on these processes [146–153]. In order to develop less costly catalysts, research has been conducted on transition metal oxides such as the nickel oxides [154–156], lithium-doped nickel oxides [157], nickel-cobalt oxides

[158,159] and cobalt–iron oxides [160]. Also examined as oxygen reduction catalysts have been the thiospinels and sulfides of transition metals [161]. However both the activity and stability of these were found to decrease after lengthy exposure to the electrolyte.

Extensive research has been directed towards the development of oxygen reduction catalysts from organic transition metal complexes.

The majority of work has concentrated on metal porphyrins [162–202], and phthalocyanines [203–233]. Early research by Jasinski on cobalt phthalocyanine [162], by Berger [136] on a variety of phthalocyanine complexes and by Alt, Binder, and Sandstede [163] on tetraphenylporphyrins illustrated the high activity these complexes possessed for oxygen reduction. Additional research by Brodd et al. [164] and others [165–176] showed, even though the activity was initially high, that it decreased with time due to a slow dissolution of the transition metal from the complex into solution. This was an irreversible process. It was reported in a review by Jahnke et al. [177] and further verified by the work of Bagotzky et al. [178] that both the stability and the activity of these metal chelates could be greatly enhanced by adsorption on to a graphite or glassy carbon surface followed by a partial pyrolysis at 900 °C. It was suggested that this heat treatment resulted in the partial pyrolysis and polymerization of the adsorbed metal chelates enhancing the activity as a result of increased stability and increased electrical conductivity. This was also suggested in the work of Meier et al. [172]. Alt et al. [163] have interpreted the activity and the mechanism on the basis of the electronic structure of the central transition metal ion. Oxygen is adsorbed on the ion and in a two-electron process it forms a peroxide intermediate. Back-bonding from the filled d_{xz} and d_{yz} orbitals of the metal ion into the anti-bonding π orbitals of the oxygen is suggested to weaken the oxygen–oxygen bond resulting in the dissociation of the peroxide intermediate. Alt et al. [163] determined that the cobalt tetraphenylporphyrins possessed higher activity, whereas Savy et al. [174] reached practically the same conclusions on the mechanism process but suggested that the iron complexes would show the higher activity.

In our laboratory, we are developing metal/air batteries and, in this context, we are studying oxygen electrodes for our air cathodes. Based in part on the previously observed behaviour of oxygen reduction on the pure-carbon electrodes as previously described, and on the enhanced activity produced by the heat treatment of the adsorbed metal chelates on the carbon electrodes, we are directing our effort towards the development of appropriate metal-doped polymer carbon electrodes. The objectives in this research were also dependent in part on the established structure and properties of polymer (glassy) carbons. Jenkins and Kawamura [234] have determined, on the basis of published information

and their own data on glassy carbons, a mechanism for the formation process and a structural model for the resulting polymer (glassy) carbon. Polymer carbon is formed from the slow pyrolysis of a highly crosslinked polymer via a constant increase in the pyrolysis temperature in an inert atmosphere. Jenkins and Kawamura [234] have suggested that the increasing temperature of pyrolysis produces a coalescence of the chain molecules in the original polymer and the formation of aromatic ribbon molecules. These ribbons have the structure of graphite sheets with carbon mainly in the trigonal form of bonding. These long, narrow, and imperfect ribbon molecules are randomly oriented and said to be tangled in a complicated manner. At temperatures above 500 °C the ribbon molecules approach each other forming intermolecular cross-links between the ribbon molecules via the elimination of hydrogen. They suggest that the process is complete at 1500 °C leaving a structure consisting of tangled aromatic ribbon molecules cross-linked by highly strained carbon–carbon covalent bonds. This process and structure is further supported by the work of Fitzer and Schafer [235] who state essentially the same conclusions but provide more detail on the pyrolysis chemistry involved.

Early studies by H.A. Pohl and Rosen [236–238] on the semiconduction properties and carrier behaviour of nickel-doped polymer carbons pointed towards possible methods of altering a carbon electrode in order to influence an electrochemical reaction. Pohl [236] reported that concentrations of nickel of the order of 1 at.% previously adsorbed within the polymer followed by pyrolysis, distinctly altered the semiconductor properties of the polymer carbons by increasing the carrier mobility. He concluded that the nickel atoms replaced some of the interplanar carbons in the graphite lattice of the ribbon molecules and acted as electron acceptors. This model would concentrate the electron at the atomically dispersed metal sites within the lattice network. He also suggested that there existed a constant fraction of bound carbons at the edges of the graphite ribbons existing as negative ions.

The oxygen-reduction reaction proceeds via adsorption of the oxygen, electron transfer from the surface sites to form the peroxide intermediates followed by subsequent electron transfers with peroxide decomposition, if one is considering a carbon electrode containing an active catalyst for the peroxide anion dissociation. This general path is indicated from all the information in the general literature. The active site should be regions of high electron concentration, a point suggested by Bockris and Srinivasan [135]. The work of Pohl et al. [236–238] suggested that this type of sites could be artificially created within the carbon lattice by atomically dispersing a transition metal within a polymer and pyrolyzing this to a temperature of from 700 to 1200 °C. Pohl dispersed the metal by adsorption

within ion-exchange resins which are highly cross-linked and would produce polymer carbons after a slow pyrolysis. This procedure resulted in the formation of polymer carbon powder, however, which when compacted with a binder could produce highly porous electrodes. The kinetics cannot be easily studied on such electrodes.

An alternative method which would yield suitable electrodes and contain the necessary electron-rich sites reported in the work of Pohl, was suggested in a paper by Adair et al. [239]. This study reported on a microscopic study of the catalytic gasification of doped carbons. They found that the carbonization of the polymer prepared from furfuryl alcohol containing known concentrations of soluble metal salt additives resulted in carbons containing atomic dispersions of metal in a metal analogous to doped semiconductors. These conclusions resulted from surface analysis by electron microscopy and the elemental analysis of the surface by the use of EDAX (energy dispersive X-ray analysis system). These conclusions were further verified by Wewerka and Imprescia [240] and Nakamizo and Walker [241], which reported on the use of organometallic additives to the polymer in a similar manner.

There were only a few reports in the literature on the possible utilization of these metal-doped polymer carbons as electrocatalysts for oxygen reduction. However Bockris and Srinivasan [135] had suggested that increased research on polymer carbons as oxygen reduction electrocatalysts was warranted. In particular, it appears that metal-doped polymer carbons show an enhanced activity for oxygen reduction in comparison with the pure-polymer carbons.

A survey on the observed behaviour of oxygen reduction on noble metal and carbon electrocatalysts has been reported in this introduction. A further review of oxygen reduction on carbon electrodes is presented in the next section. As these surveys show, the kinetics of oxygen reduction are highly dependent on the specific electrode, the synthesis procedure, induced structural alterations produced by metal additives, etc.

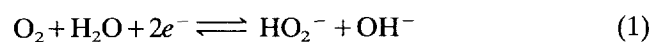
Many mechanisms are postulated in the literature to account for the reaction kinetics of oxygen reduction on noble metal and carbon electrocatalysts. In this paper, mechanisms from the literature, with additional modifications, are analysed on the assumption that Langmuir conditions of absorption are obeyed. This analysis helped us in identifying the mechanistic pathway of the oxygen-reduction reaction on our polymer carbon electrodes, as it would be reported in a future publication.

2. Oxygen reduction on carbon electrodes

Oxygen reduction on carbon electrodes has not been studied as extensively as that of oxygen reduction on

platinum electrodes. Development has mainly consisted in the use of carbon in gas diffusion electrodes [151–153] for fuel cells, serving as a porous support for active catalysts such as the noble metals [146–148]. Data from such electrodes cannot be used to establish the kinetic criteria necessary to determine the rate-determining step or possible mechanisms for the overall reaction. Another difficulty lies in the capability of fabricating the electrodes from a variety of forms of carbon such as graphite, polymer (glassy) carbons, pyrocarbons, and numerous commercially available forms of active carbons. Thus, there is no single well-defined carbon surface common to the oxygen kinetic studies which have been performed. The carbon electrodes which have been studied or tested for oxygen-reduction activity were largely characterized by their mode of preparation.

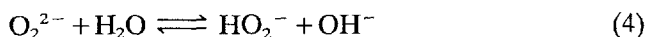
Early studies of oxygen reduction on carbon electrodes used alkaline solutions of hydrogen peroxide as electrolytes in order to investigate the relationship between hydrogen peroxide concentration and the electrode potential. One of the first of such investigations was conducted by Berl in 1943 [141]. Previous studies [242–246] reported hydrogen peroxide formation when oxygen was present during electrolysis at various metallic cathodes. An early study on oxygen reduction on a platinum electrode [247] indicated low current efficiencies and hydrogen peroxide formation. Berl [141] reasoned that the peroxide ion played an important role in oxygen reduction so he sought to use a non-corrodible carbon electrode to determine the relationship between oxygen and the peroxide ion at the equilibrium potential. Berl used porous graphite electrodes (National Carbon Company's porous graphite, grade 50) and graphite electrodes covered with an activated carbon with apparent surface area of $860 \text{ m}^2/\text{g}^{-1}$. Oxygen was forced from behind through the porous electrode into the electrolyte. The electrolyte consisted of varying concentrations of KOH and H_2O_2 . Berl found that the peroxide ion (HO_2^-) established a reversible equilibrium in alkaline solution with oxygen. The measured electrode potential (E_r) and the standard potential (E_r^0) with respect to a normal hydrogen electrode (NHE) were found to be in agreement with the values calculated from thermodynamic data for the half-cell reaction:



The equilibrium potential was found to obey the relationship:

$$E_r = E_r^0 - (RT/2F) \ln([\text{HO}_2^-][\text{OH}^-]/[\text{O}_2]) \quad (2)$$

where R is the gas constant, and F is Faraday's constant. Cathodic polarization of the electrode showed the production of hydrogen peroxide at approximately 100% current efficiency. Berl postulated the following reaction mechanism to account for his data:



A more comprehensive analysis of oxygen reduction in alkaline peroxide solutions was conducted by Yeager et al. [142]. Their objective was to obtain polarization data which would provide information concerning the kinetics of this oxygen-peroxide couple. In polarization measurements on high area porous carbon electrodes it was found that complications resulted from mass transport and distributed IR (I refers to current and R to resistance here) drops within the porous electrodes which impeded the interpretation of the overall polarization data on a kinetic basis. Yeager attempted to avoid these complications associated with electrode porosity by using relatively non-porous electrodes and relying on mass transport in the liquid phase for the transport of all reactants and products to and from the electrode surface. Several different types of carbon electrodes were used in this study. Porous graphite (type AGW, Union Carbide Corporation) was rendered virtually non-porous by filling the pore structure with molten paraffin by immersion under low pressure. A second type of carbon electrode was prepared by the vapour decomposition of a hydrocarbon on to a surface to form a pyrolytic carbon [248,249]. This type of carbon has very little porosity, a high density, and a very high degree of preferred orientation with the layer structure parallel to the surface.

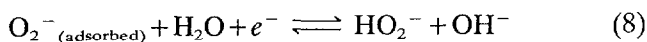
Polarization data were obtained by using both static electrode measurements and measurements on a rotating disc electrode. Both galvanostatic and potentiostatic scanning methods were used to obtain polarization data. Plots of potential versus $\log[i(i' - i)]$ were used to obtain the kinetic parameters and the concentration dependences of the rate on oxygen, and peroxide. In the above equation, (i) refers to the current density, in this case due to diffusion limitations of the reactant from the bulk solution to the surface. Yeager [142] agreed with the conclusions of Berl [141] as to the half-cell reaction responsible for the observed equilibrium potential. As used in the following rate expression for the current density, Yeager [142] determined that the transfer coefficient (α) was (1/2):

$$i = (i^0) \exp(\alpha F \eta / RT) \quad (5)$$

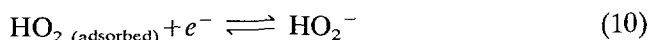
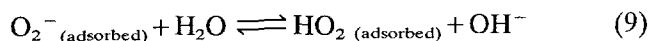
In this expression, i^0 refers to the exchange current density and η to the cathodic overpotential:

$$\eta = E_r^0 - E \quad (6)$$

Yeager [142] failed to report on the concentration dependences. He proposed the following mechanism but did not speculate on the possible rate-determining step (RDS)



This was the first reported use of an adsorbed O_2^- ion intermediate to explain oxygen reduction on a carbon electrode. Yeager also suggested that Eq. (8) of this mechanism could occur in the following two steps:



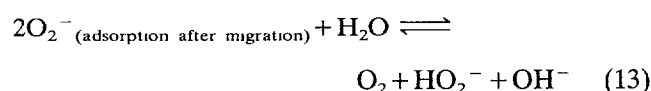
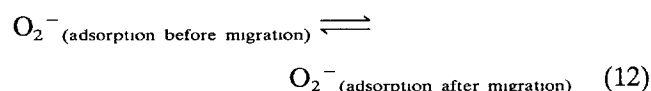
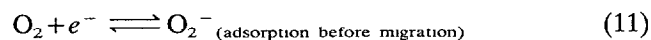
The limiting current was reported to be first order with respect to the HO_2^- concentration but zero order with respect to the OH^- concentration.

Berl [141] reported a standard electrode potential (E_r^0) of -0.0416 V versus NHE for the oxygen-peroxide ion couple in 1.0 M KOH. Yeager [142] reported a value of -0.048 V versus NHE as the E_r^0 . Bagotsky [250] obtained an E_r^0 value of -0.045 V versus NHE from their studies of the oxygen-peroxide ion couple on mercury. These values were in some contradiction with the value of -0.076 V versus NHE as calculated by both Latimer [251] and Berl [141] from known thermodynamic data. Yeager [142] concluded that the value calculated by Latimer was open to question. No explanation for this has yet been proposed.

Isotopic studies [252] on the cathodic reduction of oxygen to peroxide ion in alkaline peroxide solutions on carbon electrodes have demonstrated clearly that all the oxygen in the HO_2^- ions originated from the oxygen in solution. Additionally it has been shown in these studies that both of the oxygen atoms in HO_2^- originate from the same O_2 molecule. In this instance, however, no peroxide decomposing catalysts were present on the electrode surface.

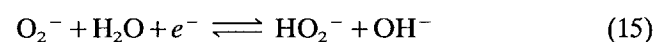
One of the most extensive kinetics investigations of oxygen reduction of carbon was conducted by Taylor and Humffray [143,144]. This large investigation utilized both static and rotating disc electrodes of glassy carbon. A rotating ring-disc study was also conducted. The investigations were conducted in a pH range of 10 to 14. Potentiostatic polarization measurements were conducted using a polished glassy carbon electrode in rotating disc and rotating ring-disc systems in alkaline KOH electrolyte, containing no added hydrogen peroxide. Tests were also conducted on glassy carbon disc electrodes which has been anodized at potentials positive to that of the observed equilibrium potential in oxygen saturated solution. It was concluded that on the non-anodized electrode, oxygen reduction proceeded via a two-electron process to peroxide ion and hydroxyl ion formation. This was the equilibrium established in the earlier study by Berl [141]. The reduction rate was found to be first order with respect to oxygen and zero order in hydroxyl ion (at constant potential with respect to a NHE). Polarization curves were also conducted

in solutions of peroxide concentrations of zero to 0.0035 M (which is comparable to the solubility of oxygen in this solution). It was found that in this range of concentration the reaction order was zero with respect to the peroxide ion concentration. The transfer coefficient was reported to be 1. Partial analysis of the anodized electrodes indicated an additional parallel reaction of a four-electron reduction of oxygen but which constituted only a small proportion of the overall current. The following mechanism was postulated by Taylor and Humffray [144] to account for the kinetic data for the non-anodized electrodes:



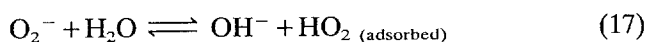
Eq. (12) was postulated as the RDS.

Interesting investigations were conducted by Appleby and co-workers [145,253] utilizing active-carbon paste ring-disc electrodes and a standardized variation of the ultra-thin porous electrode technique of Vogel and Lundquist [254]. A wide range of carbon materials (carbon blacks, graphites, active carbons) were examined. The ultra-thin electrode technique allows the porous electrode material to be treated as a planar electrode. Determination of the current in terms of A mg^{-1} of carbon yields linear Tafel plots of potential versus $\log(\text{A mg}^{-1})$. Thus, the kinetic criteria can be easily determined for oxygen reduction on porous materials. It was reported in these studies that the active carbons possessing the highest BET surface gave a transfer coefficient of 3/2 for oxygen reduction in solutions of 6 M KOH (pH=15.53). The transfer coefficient was found to decrease to 1, 2/3 and 1/2 as the pH decreased to 14, 13, and 12, respectively. For the higher area carbons the reaction was reported to be first order with respect to oxygen and zero order with respect to OH^- . The observed equilibrium potentials were not reported but from the published Tafel slopes the equilibrium potential appeared to be in the range from 900 to 960 mV versus a hydrogen electrode (HE) in the same solution of 6 M KOH for the most active carbons. The following mechanism was postulated for the oxygen reduction on the most active carbons [254]:



For a transfer coefficient of 3/2, Eq. (15) was postulated as the RDS. To give a transfer coefficient of 1, the

RDS was postulated as changing to the following:



For the transfer coefficient of 1/2, the RDS was expected to shift to Eqn. (14) of the above mechanism. They attributed this shift in the RDS as being due to a change in the surface area to electrolyte volume ratio and the water activity. It was not reported as to whether the reaction was a four-electron or two-electron reduction of oxygen.

Lack of space does not allow a further discussion of the results presented in this review. More details on these results will be treated in conjunction with the presentation of our kinetic data, to be published shortly.

3. Kinetic analysis under Langmuir conditions of adsorption

It is the purpose of this section to present an analysis of probable reaction mechanisms for oxygen reduction in alkaline solutions. Some of the mechanisms examined here are from the literature, but additional mechanisms are postulated and examined in an attempt to account for the reaction kinetics of oxygen reduction on the polymer carbon electrodes we are dealing with. Analysis of the mechanisms in this paper is made on the assumption that Langmuir conditions of adsorption are obeyed.

The basic method for the calculation of electrochemical kinetic-rate equations from a proposed mechanism is outlined in detail in several sources [1,2,20,134], so it will not be given here. Some refinements are introduced, however, so the basic equations will be briefly examined. A complete sample derivation of possible rate equations based on a proposed mechanism is given. Each mechanism and the resulting rate equations and comments are reported in a separate Table for easy reference.

In the calculation of one possible rate equation from a proposed mechanism, one of the reaction steps is assumed to have the lowest rate and is defined as the RDS for the entire reaction. The forward direction in this case is the net reduction of oxygen to four hydroxyl anions or partial reduction to the peroxide anion (HO_2^-) or hydrogen peroxide. The reaction steps before and after the RDS are assumed to be in a quasi-equilibrium state or a steady-state situation. The reaction steps possible in these mechanisms can be adsorption or desorption processes, reaction on the surface between adsorbed molecules, reaction between an adsorbed molecule and one in solution, or any of these reactions with the addition of an electron transfer.

Consider the following sample reaction step in which an oxygen molecule adsorbs on to a vacant surface site accepting an electron from the electrode in the process:



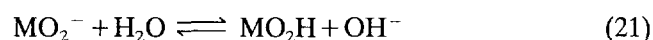
The rates for the cathodic (i_c) and the anodic (i_a) directions would be [134,255]:

$$i_c = k_{18}[M][O_2] \exp(-\beta FE/RT) \quad (19)$$

$$i_a = k_{-18}[MO_2^-] \exp\{(1-\beta)FE/RT\} \quad (20)$$

The constants k_{18} and k_{-18} are rate constants which refer to the cathodic and anodic directions of the reaction, respectively, and β is the symmetry factor for this electron-transfer step, E is the imposed electrode potential. The symmetry factor has been studied and defined by many investigators [129,134,255,256] so an in-depth discussion will not be presented here. The simplest definition, however, is that β represents the fraction of the total potential drop from the surface to the outer Helmholtz plane, which affects the activation energy for the forward or reverse rate. A decrease in the potential E , measured with respect to a NHE, will lower the activation energy for i_c , and thus increase the rate of reduction. The activation energy is hidden in the rate constant. The general consensus is that for a single electron-transfer step, the value of β is 1/2 [134,255,256]. Bockris and Reddy [134] provide the most in-depth analysis of the symmetry factor. This should not be confused with the transfer coefficient α , which is determined from the consideration of the entire mechanism, as will be shown in the full sample calculation. These equations are based on Langmuir conditions of adsorption [257]. These conditions state that the heat of adsorption (or chemisorption) of a molecule on a surface remains unaffected by the degree of total surface coverage, or that the coverage is virtually constant over the potential range studied in this case. Constant coverage with potential or concentration change usually means a coverage of less than $\theta=0.1$ or greater than $\theta=0.9$, or a mechanism which has no effect on coverage.

Surface coverage can be attributed to several factors, each of which has to be taken into consideration in the analysis of the reaction mechanism. The coverage could be due to the build-up of reaction intermediates necessary in the RDS. Consider that the second step in this mechanism is:



If this is postulated to be the RDS, then the current would be expressed by:

$$i_c = \bar{k}_{21}[H_2O][MO_2^-] \quad (22)$$

The anodic current is assumed to be non-existent for oxygen reduction, since the potential range used in the kinetic analysis is at least 280 mV cathodic to the equilibrium potential of the oxygen-reduction reaction. The concentration of water is taken as constant within

the outer Helmholtz plane so, Eq. (22) reduces to:

$$i_c = \bar{k}_{21}[MO_2^-] \quad (23)$$

In the extreme case, one could say that all the sites at which oxygen reduction can occur are occupied by the adsorbed O_2^- , which would lead to the potential independent rate equation:

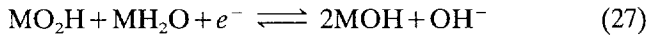
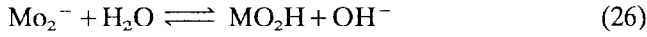
$$i_c = \bar{k}_{21}[MO_2^-]^0 \quad (24)$$

In general, $[MA]^0$ will refer to a saturated or constant surface concentration of adsorbed species MA, in this case MO_2^- . This does not necessarily mean that the entire electrode surface is saturated with chemisorbed O_2^- . Only a very small fraction of surface sites may be capable of sustaining oxygen reduction at a given potential, such that total coverage of these sites may occupy only a small fraction of the surface. Thus, the idea of active surface sites is introduced. What constitutes the basis of an active site has been the subject of much debate in the fields of catalysis and electrocatalysis [124-128,130-132,135,136]. Both the investigation of geometric and electronic factors in electrochemical reactions on noble metal electrodes has been thoroughly investigated, yet no sound and consistent conclusions can be drawn. Suffice is to say, that one must consider the possibility that only a small fraction of surface sites exists possessing the ability to influence the rate of oxygen reduction. In this case, the entire surface coverage of all species on the electrode could remain constant, thereby satisfying Langmuir conditions; yet zero to total blockage of the active sites could occur. For this reason, the concentration of surface sites $[M]$ may not remain constant with potential or changes in pH or oxygen concentration. Any possibility of change in $[M]$ and its effect on the resulting kinetics should be explicitly examined, even if the total coverage on the electrode surface remains virtually constant.

In order to effectively analyse the effect of $[M]$ on the derivation of the rate kinetics from the proposed mechanisms, consideration must be given to exactly what constitutes surface coverage. Each possibility would have a different effect on the kinetic via the occupation of the active sites. Only the active sites need be occupied by a non-mobile chemisorbed intermediate.

Chemisorption refers to an actual chemical interaction of the adsorbed species with one or more surface atoms. With an electron transfer some interaction is assured. The chemisorbed molecule is then much more immobile than that of physically adsorbed molecules, such as water. In the present example, complete saturation of the active sites as in Eqs. (21) and (24) would produce a limiting current density, independent of potential and oxygen concentration. This would hold true up to the potential at which oxygen reduction could occur on even the inactive sites.

The analysis is continued on this example mechanism with the assumption that the coverage of intermediate species on the surface sites, whether active or not, is such that [M] is essentially constant. Below is the entire mechanism to be examined, suggested as a modified peroxide path, no. 1:



If Eq. (25) is assumed to be the RDS and $\beta = 1/2$, then the current can be expressed as:

$$i_c = k_{25}[M][O_2] \exp(-FE/2RT) \quad (29)$$

For oxygen reduction, $i = i_c$. This gives mechanistic criteria of $\alpha = 1/2$, and reaction orders with respect to $[OH^-]$ and $[O_2]$ of 0 and 1, respectively.

With the assumption that Eq. (26) is the RDS, and the assumption that Eq. (25) is in a quasi-equilibrium, the current can be expressed as Eq. (32) by the following derivation:

$$k_1[M][O_2] \exp(-\beta FE/2RT) = k_{-1}[MO_2^-] \exp((1-\beta)FE/RT) \quad (30)$$

Substituting for $[MO_2^-]$ in Eq. (23) from the above equilibrium established in step (25) gives:

$$[MO_2^-] = (k_{25}/k_{-25})[M][O_2] \exp(-FE/RT) \quad (31)$$

$$i = \bar{k}_{21}\bar{k}_{25}[M][O_2] \exp(-FE/RT) \quad (32)$$

where \bar{k}_{25} , k_{25}/k_{-25} is the equilibrium constant for Eq. (25). This gives the mechanistic criteria of $\alpha = 1$, and the reaction orders with respect to $[OH^-]$ and $[O_2]$ of 0 and 1, respectively.

With the assumption that Eq. (27) is the RDS, and that Eqs. (25) and (26) are in quasi-equilibrium:

$$i = \bar{k}_{27}[MO_2H] \exp(-\beta FE/RT) \quad (33)$$

$$[MO_2H] = \bar{k}_{26}[MO_2^-][OH^-] \quad (34)$$

Insertation of Eq. (31) for $[MO_2^-]$ gives:

$$[MO_2H] = \bar{k}_{26}\bar{k}_{25}[M][O_2][OH^-]^{-1} \exp(-FE/RT) \quad (35)$$

Insertation of Eq. (35) into Eq. (33) with $\beta = 1/2$ gives the following Eq. for the current density:

$$i = \bar{k}_{27}\bar{k}_{26}\bar{k}_{25}[M][OH^-]^{-1}[O_2] \exp(-3FE/2RT) \quad (36)$$

where $\bar{k}_{26} = k_{26}/k_{-26}$ and \bar{k}_{27} refer to the rate constant for Eq. (27). This gives the mechanistic criteria of $\alpha = 3/2$, and the reaction orders with respect to $[OH^-]$ and $[O_2]$ of -1 and 1 , respectively.

With the assumption that Eq. (28) is the RDS, and that Eqs. (25), (26) and (27) are in quasi-equilibrium, then:

$$i = \bar{k}_{28}[MOH] \exp[-\beta FE/RT] \quad (37)$$

$$[MOH] = \bar{k}_{27}^{1/2}[MO_2H]^{1/2}[OH^-]^{-1/2} \exp[-FE/2RT] \quad (38)$$

Insertion of Eq. (35) for $[MO_2H]$ gives:

$$[MOH] = \{\bar{k}_{27}\bar{k}_{26}\bar{k}_{25}[M]\}^{1/2}[OH^-]^{-1}[O_2]^{1/2} \times \exp(-FE/RT) \quad (39)$$

Substitution of Eq. (39) into Eq. (37) with $\beta = 1/2$, will yield the following Eq. for current density:

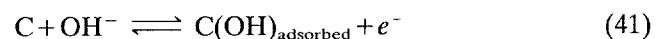
$$i = \bar{k}_{28}\{\bar{k}_{27}\bar{k}_{26}\bar{k}_{25}[M]\}^{1/2}[OH^-]^{-1}[O_2]^{1/2} \times \exp(-3FE/2RT) \quad (40)$$

where $\bar{K}_{27} = k_{27}/k_{-27}$ and \bar{K}_{28} refers to the rate constant for Eq. (28). Henceforth, the subscript n in K_n or k_n refers to step number n in the proposed mechanism with $K_n = k_n/k_{-n}$. Eq. (40) gives the mechanistic criteria of $\alpha = 3/2$, and the reaction orders with respect to $[OH^-]$ and $[O_2]$ of -1 and $1/2$, respectively.

In these calculations, the concentration of vacant surface sites on which the reaction can occur is explicitly denoted in the equations by [M]. The mechanistic criteria just calculated are dependent upon the condition that [M] remains constant over the potential range, conditions of pH, and $[O_2]$ present during our experimental measurements. Saturation of the surface sites by reaction intermediates was not expected to occur under the experimental conditions used in these tests. Therefore, in the forthcoming mechanisms, there is no further investigation of surface-site coverage by this means.

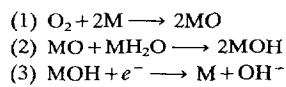
Another means of surface-site blockage or coverage which does have to be examined is coverage through a separate potential-dependent equilibrium reaction, which in no way is dependent on oxygen concentration. One possibility is that the coverage is caused by chemisorbed hydroxyl groups. Such an hypothesis was used by Damjanovic and Brusic [2] to account for the oxygen-reduction kinetics on oxide-free platinum in acid or alkaline electrolyte. In order to account for the surface-coverage data, the coverage was postulated as being due to the potential-dependent equilibrium reaction (28).

Zolotova and Gants [137] used potentiostatic charging curves to examine coverage on pyrolytic graphite anodes in alkaline electrode. They and other investigators [258,259] suggested the formation of adsorption layers on carbon by the equilibrium:



Work by Zoltowski [152], using chronovoltammetry and cyclic chronopotentiometry on active carbons in acid and alkaline electrolytes, led him to postulate that two oxidation processes take place on the carbon surface at potentials exceeding 800 mV/HE. One leads to the formation of oxygen-containing redox surface groups on the carbon, and the other to oxygen adsorbed on the surface in a form which can be reduced only at much lower potentials. Other authors have also postulated the presence of certain redox surface groups on the carbon surface [138,139,149]. Based on these previous studies, two equilibrium potential-dependent reactions are suggested, which could affect the reaction kinetics of oxygen reduction by blockage of necessary surface sites. The first possibility is coverage by adsorbed

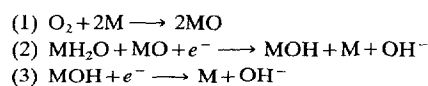
Table 1
The oxide path [260]



RDS no. ^a	Calculated rate equations			
(1)	$i = k_1[\text{M}]^2[\text{O}_2]$			
(2)	$i = k_2(k_1)^{1/2}[\text{M}][\text{O}_2]^{1/2}$			
(3)	$i = k_3(k_2k_1)^{1/2}[\text{MH}_2\text{O}]^{1/2}[\text{M}]^{1/2}[\text{O}_2]^{1/4} \exp(-FE/2RT)$			
Coverage conditions	RDS no.	α	$[\text{OH}^-]^m$ <i>m</i>	$[\text{O}_2]^p$ <i>p</i>
[M] _{constant} [MOH] _{equilibrium}	(1)	0	0	1
	(2)	0	0	1/2
	(3)	1/2	0	1/4
[M] _{low} [MOH] _{equilibrium}	(1)	2	-2	1
	(2)	1	-1	1/2
	(3)	3/2	-1	1/4

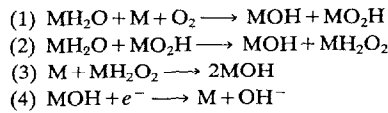
^aRDS = rate-determining step

Table 2
The electrochemical oxide path [260]



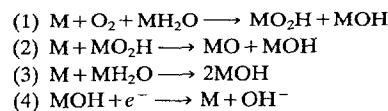
RDS no.	Calculated rate equations			
(1)	$i = k_1[\text{M}]^2[\text{O}_2]$			
(2)	$i = k_2(k_1)^{1/2}[\text{MH}_2\text{O}][\text{M}][\text{O}_2]^{1/2} \exp(-FE/2RT)$			
(3)	$i = k_3k_2(k_1)^{1/2}[\text{MH}_2\text{O}][\text{OH}^-]^{-1}[\text{O}_2]^{1/2} \exp(-3FE/2RT)$			
Coverage conditions	RDS no.	α	$[\text{OH}^-]^m$ <i>m</i>	$[\text{O}_2]^p$ <i>p</i>
[M] _{constant} [MOH] _{equilibrium}	(1)	0	0	1
	(2)	1/2	0	1/2
	(3)	3/2	-1	1/2
[M] _{low} [MOH] _{equilibrium}	(1)	2	-2	1
	(2)	5/2	-2	1/2
	(3)	5/2	-2	1/2

Table 3
The hydrogen peroxide path [260]



RDS no.	Calculated rate equations			
(1)	$i = k_1[\text{MH}_2\text{O}][\text{M}][\text{O}_2]$			
(2)	$i = k_2k_4k_1[\text{MH}_2\text{O}]^2[\text{OH}^-]^{-1}[\text{O}_2] \exp(-FE/RT)$			
(3)	$i = k_3(k_4)^2k_2k_1[\text{MH}_2\text{O}]^2[\text{OH}^-]^{-2}[\text{O}_2] \exp(-2FE/RT)$			
(4)	$i = k_4\{k_3k_2k_1[\text{MH}_2\text{O}]^2[\text{M}]^2\}^{1/4}[\text{O}_2]^{1/4} \exp(-FE/2RT)$			
Coverage conditions	RDS no.	α	$[\text{OH}^-]^m$ <i>m</i>	$[\text{O}_2]^p$ <i>p</i>
[M] _{constant} [MOH] _{equilibrium}	(1)	0	0	1
	(2)	1	-1	1
	(3)	2	-2	1
	(4)	1/2	0	1/4
[M] _{low} [MOH] _{equilibrium}	(1)	1	-1	1
	(2)	3	-3	1
	(3)	4	-4	1
	(4)	3/2	-1	1/4

Table 4
The metal peroxide path [260]



RDS no.	Calculated rate equations			
(1)	$i = k_1[\text{MH}_2\text{O}][\text{M}][\text{O}_2]$			
(2)	$i = k_4k_2k_1[\text{MH}_2\text{O}][\text{M}][\text{OH}^-]^{-1}[\text{O}_2] \exp(-FE/RT)$			
(3)	$i = (k_4)^2k_3k_2k_1[\text{MH}_2\text{O}]^2[\text{OH}^-]^{-2}[\text{O}_2] \exp(-2FE/RT)$			
(4)	$i = k_4\{k_3k_2k_1[\text{MH}_2\text{O}]^2[\text{M}]^2\}^{1/4}[\text{O}_2]^{1/4} \exp(-FE/2RT)$			
Coverage conditions	RDS no.	α	$[\text{OH}^-]^m$ <i>m</i>	$[\text{O}_2]^p$ <i>p</i>
[M] _{constant} [MOH] _{equilibrium}	(1)	0	0	1
	(2)	1	-1	1
	(3)	2	-2	1
	(4)	1/2	0	1/4
[M] _{low} [MOH] _{equilibrium}	(1)	2	-2	1
	(2)	3	-3	1
	(3)	4	-4	1
	(4)	3/2	-1	1/4

hydroxyl groups, as suggested by Damjanovic and Zolotova (Eq. (28)).

At each potential an equilibrium coverage is achieved so that the rates of desorption and adsorption are equal and that Langmuir conditions prevail. This gives:

$$\begin{aligned} k_d[\text{MOH}] \exp(-\beta FE/RT) \\ = k_a[\text{M}][\text{OH}^-] \exp\{(1-\beta)FE/RT\} \end{aligned} \quad (42)$$

Table 5
The electrochemical metal peroxide path [260]

(1) $M + O_2 + MH_2O \longrightarrow MOH + MO_2H$ (2) $MO_2H + e^- \longrightarrow MO + OH^-$ (3) $MO + MH_2O \longrightarrow 2MOH$ (4) $MOH + e^- \longrightarrow M + OH^-$				
RDS Calculated rate equations no.				
(1) $i = k_1[MH_2O][M][O_2]$ (2) $i = k_2k_4k_1[MH_2O][OH^-]^{-1}[O_2] \exp(-3FE/2RT)$ (3) $i = k_3k_4k_2k_1[MH_2O]^2[OH^-]^{-2}[O_2] \exp(-2FE/RT)$ (4) $i = k_4\{k_3k_2k_1[MH_2O]^2[M]\}^{1/3}[OH^-]^{-1/3}[O_2]^{1/3} \exp(-5FE/6RT)$				
Coverage conditions	RDS no	α	$[OH^-]^m$ <i>m</i>	$[O_2]^p$ <i>p</i>
$[M]_{constant}$	(1)	0	0	1
$[MOH]_{equilibrium}$	(2)	3/2	-1	1
	(3)	2	-2	1
	(4)	5/6	-1/3	1/3
$[M]_{low}$ $[MOH]_{equilibrium}$	(1)	2	-2	1
	(2)	5/2	-2	1
	(3)	4	-4	1
	(4)	11/6	-4/3	1/3

Table 6
The alkaline path [261]

(1) $M + O_2 + 2e^- \longrightarrow MO_2^{2-}$ (2) $M + MO_2^{2-} + 2H_2O \longrightarrow 2MH_2O_2^-$ (3) $MH_2O_2^- \longrightarrow MOH + OH^-$ (4) $MOH + e^- \longrightarrow M + OH^-$				
RDS no Calculated rate equations				
(1) $i = k_1[M][O_2] \exp(-FE/RT)$ (2) $i = k_2k_1[M]^2[O_2] \exp(-2FE/RT)$ (3) $i = k_3(k_2k_1)^{1/2}[M][O_2]^{1/2} \exp(-FE/RT)$ (4) $i = k_4k_3(k_2k_1)^{1/2}[M][OH^-]^{-1}[O_2]^{1/2} \exp(-3FE/2RT)$				
Coverage conditions	RDS no	α	$[OH^-]^m$ <i>m</i>	$[O_2]^p$ <i>p</i>
$[M]_{constant}$ $[MOH]_{equilibrium}$	(1)	1	0	1
	(2)	2	0	1
	(3)	1	0	1/2
	(4)	3/2	-1	1/2
$[M]_{low}$ $[MOH]_{equilibrium}$	(1)	2	-1	1
	(2)	4	-2	1
	(3)	2	-1	1/2
	(4)	5/2	-2	1/2

In this case, k_a and k_d refer to the rate constants for adsorption and desorption, respectively. $K_c = k_d/k_a$ and is referred to as the equilibrium constant for the coverage reaction. In terms of the fraction of the surface covered by the hydroxyl groups, θ , and the fraction occupied by adsorbed H_2O , $(1 - \theta)$, $[MOH] = \theta[M]^0$ and $[M] = (1 - \theta)[M]^0$. Solving for $[MOH]$ from the equilibrium above gives:

Table 7
Path suggested by Conway and Bourgault [262]

(1) $M + O_2 + MH_2O \longrightarrow MO_2H + MOH$ (2) $MO_2H \longrightarrow MOH + MO$ (3) $MO + H_2O + e^- \longrightarrow MOH + OH^-$ (4) $MOH + e^- \longrightarrow M + OH^-$				
RDS Calculated rate equations no.				
(1) $i = k_1[MH_2O][M][O_2]$ (2) $i = k_2k_4k_1[MH_2O][OH^-]^{-1}[O_2] \exp(-FE/RT)$ (3) $i = k_3(k_4)^2k_2k_1[MH_2O][M]^{-1}[OH^-]^{-2}[O_2] \exp(-5FE/2RT)$ (4) $i = k_4\{k_3k_2k_1[MH_2O][M]\}^{1/3}[OH^-]^{-1/3}[O_2]^{1/3} \exp(-5FE/6RT)$				
Coverage conditions	RDS no.	α	$[OH^-]^m$ <i>m</i>	$[O_2]^p$ <i>p</i>
$[M]_{constant}$	(1)	0	0	1
$[MOH]_{equilibrium}$	(2)	1	-1	1
	(3)	5/2	-2	1
	(4)	5/6	-1/3	1/3
$[M]_{low}$ $[MOH]_{equilibrium}$	(1)	2	-2	1
	(2)	2	-2	1
	(3)	5/2	-2	1
	(4)	3/2	-1	1/3

Table 8
Alternative path of Conway and Bourgault [262]

(1) $M + MH_2O + O_2 \longrightarrow MOH + MO_2H$ (2) $MO_2H + e^- \longrightarrow MO + OH^-$ (3) $MO + H_2O + e^- \longrightarrow MOH + OH^-$ (4) $MOH + e^- \longrightarrow M + OH^-$				
RDS Calculated rate equations no				
(1) $i = k_1[MH_2O][M][O_2]$ (2) $i = k_2k_4k_1[MH_2O][OH^-]^{-1}[O_2] \exp(-3FE/2RT)$ (3) $i = k_3k_4k_2k_1[MH_2O][OH^-]^{-2}[O_2] \exp(-5FE/2RT)$ (4) $i = k_4\{k_3k_2k_1[MH_2O][M]\}^{1/2}[OH^-]^{-1}[O_2]^{1/2} \exp(-3FE/2RT)$				
Coverage conditions	RDS no.	α	$[OH^-]^m$ <i>m</i>	$[O_2]^p$ <i>p</i>
$[M]_{constant}$ $[MOH]_{equilibrium}$	(1)	0	0	1
	(2)	3/2	-1	1
	(3)	5/2	-2	1
	(4)	3/2	-1	1/2
$[M]_{low}$ $[MOH]_{equilibrium}$	(1)	2	-2	1
	(2)	5/2	-2	1
	(3)	7/2	-3	1
	(4)	5/2	-2	1/2

$$[MOH] = k_c^{-1}[M][OH^-] \exp(FE/RT) \tag{43}$$

Expressing $[MOH]$ and $[M]$ in terms of the maximum amount of surface sites available for coverage $[M]^0$ gives:

$$\theta = 1/\{1 + k_c[OH^-]^{-1} \exp(-FE/RT)\} \tag{44}$$

Table 9
Path suggested by Riddiford [263]

(1)	$O_2 + MH_2O + e^- \longrightarrow MO_2H + OH^-$			
(2)	$MO_2H + e^- \longrightarrow MO + OH^-$			
(3)	$MO + MH_2O \longrightarrow 2MOH$			
(4)	$MOH + e^- \longrightarrow M + OH^-$			
RDS no	Calculated rate equations			
(1)	$i = k_1[MH_2O][O_2] \exp(-FE/2RT)$			
(2)	$i = k_2k_1[MH_2O][OH^-]^{-1}[O_2] \exp(-3FE/2RT)$			
(3)	$i = k_3k_2k_1[MH_2O]^2[OH^-]^{-2}[O_2] \exp(-2FE/RT)$			
(4)	$i = k_4(k_3k_2k_1)^{1/2}[MH_2O][OH^-]^{-1}[O_2]^{1/2} \exp(-3FE/2RT)$			
Coverage conditions	RDS no.	α	$[OH^-]^m$ <i>m</i>	$[O_2]^p$ <i>p</i>
$[M]_{\text{constant}}$	(1)	1/2	0	1
$[MOH]_{\text{equilibrium}}$	(2)	3/2	-1	1
	(3)	2	-2	1
	(4)	3/2	-1	1/2
$[M]_{\text{low}}$	(1)	3/2	-1	1
$[MOH]_{\text{equilibrium}}$	(2)	5/2	-2	1
	(3)	4	-4	1
	(4)	5/2	-2	1/2

Table 10
Krasilshchikov's path [264]

(1)	$2M + O_2 \longrightarrow 2MO$			
(2)	$MO + e^- \longrightarrow MO^-$			
(3)	$MO^- + H_2O \longrightarrow MOH + OH^-$			
(4)	$MOH + e^- \longrightarrow M + OH^-$			
RDS no.	Calculated rate equations			
(1)	$i = k_1[M]^2[O_2]$			
(2)	$i = k_2(k_1)^{1/2}[M][O_2]^{1/2} \exp(-FE/2RT)$			
(3)	$i = k_3k_2(k_1)^{1/2}[M][O_2]^{1/2} \exp(-FE/RT)$			
(4)	$i = k_4k_3k_2(k_1)^{1/2}[M][OH^-]^{-1}[O_2]^{1/2} \exp(-3FE/2RT)$			
Coverage conditions	RDS no.	α	$[OH^-]^m$ <i>m</i>	$[O_2]^p$ <i>p</i>
$[M]_{\text{constant}}$	(1)	0	0	1
$[MOH]_{\text{equilibrium}}$	(2)	1/2	0	1/2
	(3)	1	0	1/2
	(4)	3/2	-1	1/2
$[M]_{\text{low}}$	(1)	2	-2	1
$[MOH]_{\text{equilibrium}}$	(2)	3/2	-1	1/2
	(3)	2	-1	1/2
	(4)	5/2	-2	1/2

$$[MOH] = [M]^0 / \{1 + k_c[OH^-]^{-1} \exp(-FE/RT)\} \quad (45)$$

$$[M] = \{[M]^0 k_c [OH^-]^{-1} \times \exp(-FE/RT)\} / \{1 + k_c[OH^-]^{-1} \exp(-FE/RT)\} \quad (46)$$

The second form of coverage suggested is that, due to chemisorbed oxygen atoms, which could account for the observations of Zoltowski [152] of adsorbed oxygen in a form more difficult to reduce.

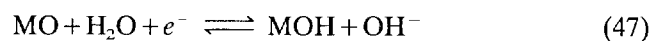
Table 11
Wade and Hackerman's path [265]

(1)	$2M + MH_2O + O_2 + 2e^- \longrightarrow 2MOH^- + MO$			
(2)	$MO + MH_2O + 2e^- \longrightarrow 2MOH^-$			
RDS no	Calculated rate equations			
(1)	$i = k_1[M]^2[MH_2O][O_2] \exp(-FE/RT)$			
(2)	$i = k_2k_1[MH_2O]^2[M]^2[MOH^-]^{-2}[O_2] \exp(-3FE/RT)$			
Coverage conditions	RDS no.	α	$[OH^-]^m$ <i>m</i>	$[O_2]^p$ <i>p</i>
$[M]_{\text{constant}}$	(1)	1	0	1
	(2)	3	-2	1
$[M]_{\text{low}}$	(1)	4	-3	1
	(2)	7	-6	1

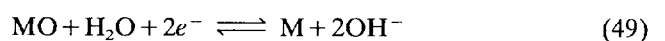
Table 12
Path 1 suggested by Damjanovic [266]

(1)	$M + H_2O + O_2 + e^- \longrightarrow MO_2H + OH^-$			
(2)	$MO_2H + e^- \longrightarrow MO + OH^-$			
(3)	$MO + H_2O + e^- \longrightarrow MOH + OH^-$			
(4)	$MOH + e^- \longrightarrow M + OH^-$			
RDS no.	Calculated rate equations			
(1)	$i = k_1[M][O_2] \exp(-FE/2RT)$			
(2)	$i = k_2k_1[M][OH^-]^{-1}[O_2] \exp(-3FE/2RT)$			
(3)	$i = k_3k_2k_1[M][OH^-]^{-2}[O_2] \exp(-5FE/2RT)$			
(4)	$i = k_4k_3k_2k_1[M][OH^-]^{-3}[O_2] \exp(-7FE/2RT)$			
Coverage conditions	RDS no.	α	$[OH^-]^m$ <i>m</i>	$[O_2]^p$ <i>p</i>
$[M]_{\text{constant}}$	(1)	1/2	0	1
$[MOH]_{\text{equilibrium}}$	(2)	3/2	-1	1
	(3)	5/2	-2	1
	(4)	7/2	-3	1
$[M]_{\text{low}}$	(1)	3/2	-1	1
$[MOH]_{\text{equilibrium}}$	(2)	5/2	-2	1
	(3)	7/2	-3	1
	(4)	9/2	-4	1

Such an equilibrium coverage would consist of the following two steps:



Addition of these steps gives the net equilibrium reaction:



At equilibrium the rates of adsorption and desorption are equal:

$$k_a[MO] \exp(-2\beta FE/RT) = k_d[M][OH^-]^2 \exp\{2(1-\beta)FE/RT\} \quad (50)$$

Rearranging yields:

Table 13
Path 2 suggested by Damjanovic [266]

(1)	$2M + O_2 \longrightarrow 2MO$			
(2)	$MO + H_2O \longrightarrow MO-H-OH$			
(3)	$MO-H-OH + e^- \longrightarrow MO-H-OH^-$			
(4)	$MO-H-OH^- \longrightarrow MOH + OH^-$			
(5)	$MOH + e^- \longrightarrow M + OH^-$			
RDS no	Calculated rate equations			
(1)	$i = k_1[M]^2[O_2]$			
(2)	$i = k_2(k_1)^{1/2}[M][O_2]^{1/2}$			
(3)	$i = k_3k_2(k_1)^{1/2}[M][O_2]^{1/2} \exp(-FE/2RT)$			
(4)	$i = k_4k_3k_2(k_1)^{1/2}[M][O_2]^{1/2} \exp(-FE/RT)$			
(5)	$i = k_5k_4k_3k_2(k_1)^{1/2}[M][OH^-]^{-1}[O_2]^{1/2} \exp(-3FE/2RT)$			
Coverage conditions	RDS no.	α	$[OH^-]^m$ <i>m</i>	$[O_2]^p$ <i>p</i>
$[M]_{\text{constant}}$	(1)	0	0	1
$[MOH]_{\text{equilibrium}}$	(2)	0	0	1/2
	(3)	1/2	0	1/2
	(4)	1	0	1/2
	(5)	3/2	-1	1/2
$[M]_{\text{low}}$	(1)	2	-2	1
	(2)	1	-1	1/2
$[MOH]_{\text{equilibrium}}$	(3)	3/2	-1	1/2
	(4)	2	-1	1/2
	(5)	5/2	-2	1/2

Table 14
Path 3 suggested by Damjanovic [266]

(1)	$M + H_2O + O_2 + e^- \longrightarrow MO_2H + OH^-$			
(2)	$MO_2H + e^- \longrightarrow MO + OH^-$			
(3)	$MO + H_2O \longrightarrow MO-H-OH$			
(4)	$MO-H-OH + e^- \longrightarrow MO-H-OH^-$			
(5)	$MO-H-OH^- \longrightarrow MOH + OH^-$			
(6)	$MOH + e^- \longrightarrow M + OH^-$			
RDS no	Calculated rate equations			
(1)	$i = k_1[M][O_2] \exp(-FE/2RT)$			
(2)	$i = k_2k_1[M][OH^-]^{-1}[O_2] \exp(-3FE/2RT)$			
(3)	$i = k_3k_2k_1[M][OH^-]^{-2}[O_2] \exp(-2FE/RT)$			
(4)	$i = k_4k_3k_2k_1[M][OH^-]^{-2}[O_2] \exp(-5FE/2RT)$			
(5)	$i = k_5k_4k_3k_2k_1[M][OH^-]^{-2}[O_2] \exp(-3FE/RT)$			
(6)	$i = k_6k_5k_4k_3k_2k_1[M][OH^-]^{-3}[O_2] \exp(-7FE/2RT)$			
Coverage conditions	RDS no	α	$[OH^-]^m$ <i>m</i>	$[O_2]^p$ <i>p</i>
$[M]_{\text{constant}}$	(1)	1/2	0	1
$[MOH]_{\text{equilibrium}}$	(2)	3/2	-1	1
	(3)	2	-2	1
	(4)	5/2	-2	1
	(5)	3	-2	1
	(6)	7/2	-3	1
	$[M]_{\text{low}}$	(1)	3/2	-1
$[MOH]_{\text{equilibrium}}$	(2)	5/2	-2	1
	(3)	3	-3	1
	(4)	7/2	-3	1
	(5)	4	-3	1
	(6)	9/2	-4	1

$$[MO] = k_c[M][OH^-]^2 \exp(2FE/RT) \quad (51)$$

If the fraction of available sites covered by oxygen atoms is represented by θ , then $[MO] = \theta[MO]^0$ and $[M] = (1 - \theta)[M]^0$; therefore, substitution into Eq. (51) yields:

$$\theta = 1 / \{1 + k_c[OH^-]^{-2} \exp(-2FE/RT)\} \quad (52)$$

$$[MO] = [M]^0 / \{1 + k_c[OH^-]^{-2} \exp(-2FE/RT)\} \quad (53)$$

$$[M] = \{[M]^0 k_c [OH^-]^{-2} \times \exp(-2FE/RT)\} / \{1 + k_c [OH^-]^{-2} \exp(-2FE/RT)\} \quad (54)$$

Eqs. (46) and (54) represent two processes which could affect the concentration of vacant sites and the reaction kinetics derived from the mechanisms. Depending on the values of k_c , pH, and potential, substitution of either Eq. (46) or Eq. (54) for $[M]$ in the previously derived rate equations could distinctly alter the expected mechanistic criteria. In the case of low surface coverage or of saturation of the surface with adsorbed species independent of the oxygen-reduction reaction, there can be a potential range in which the coverage does not vary. This range would depend on the values of k_c and pH. In this case, the concentration of vacant sites is constant, so $[M] = [M]^0$ or $[M] = f[M]^0$, where f is a constant. No changes in the mechanistic criteria will occur.

In the case of high surface coverage, it is possible for the coverage to depend on the potential. For the extreme case in which $k_c[OH^-]^{-1} \exp(-FE/RT)$ is much less than 1, Eq. (46) would reduce to:

$$[M] = [M]^0 k_c [OH^-]^{-1} \exp(-FE/RT) \quad (55)$$

It should be noted from Eq. (46), that a transition from a low concentration of vacant sites to a condition of high concentration of vacant sites can be achieved either by a decrease in $[OH^-]$ or a decrease in potential E . Substitution of Eq. (55) into Eqs. (29), (32), (36) and (40) will alter each rate law and the resulting mechanism criteria.

Substitution of Eq. (55) into Eq. (29) yields:

$$i = \tilde{k}_{25} k_c [M]^0 [OH^-]^{-1} [O_2] \exp(-3FE/2RT) \quad (56)$$

This gives new mechanistic criteria of $\alpha = 3/2$, and reaction orders with respect to $[OH^-]$ and $[O_2]$ of -1 and 1 , respectively.

Substitution of Eq. (55) into Eq. (32) yields:

$$i = \tilde{k}_{21} \tilde{k}_{25} k_c [M]^0 [OH^-]^{-1} [O_2] \exp(-2FE/RT) \quad (57)$$

This gives new mechanistic criteria of $\alpha = 2$, and reaction orders with respect to $[OH^-]$ and $[O_2]$ of -1 and 1 , respectively.

Substitution of Eq. (55) into Eq. (36) yields:

Table 15
The Hoare path [267]

(1) $M + O_2 \longrightarrow MO_2$	(2) $MO_2 + e^- \longrightarrow MO_2^-$	(3) $MO_2^- + H_2O \longrightarrow MO_2H + OH^-$	(4) $MO_2H + e^- \longrightarrow MO_2H^-$	(5) $MO_2H^- + H_2O \longrightarrow MH_2O_2 + OH^-$	(6) $2MH_2O_2 \longrightarrow M + 2H_2O + MO_2$
RDS no.	Calculated rate equations				
(1)	$i = k_1[M][O_2]$				
(2)	$i = k_2k_1[M][O_2] \exp(-FE/2RT)$				
(3)	$i = k_3k_2k_1[M][O_2] \exp(-FE/RT)$				
(4)	$i = k_4k_3k_2k_1[M][OH^-]^{-1}[O_2] \exp(-3FE/2RT)$				
(5)	$i = k_5k_4k_3k_2k_1[M][OH^-]^{-1}[O_2] \exp(-2FE/RT)$				
(6)	$i = k_6\{k_3k_4k_3k_2k_1[M]\}^2[OH^-]^{-4}[O_2]^2 \exp(-4FE/RT)$				
Coverage conditions	RDS no.	α	$[OH^-]^m$	$[O_2]^p$	
$[M]_{\text{constant}}$ $[MOH]_{\text{equilibrium}}$	(1)	0	0	1	
	(2)	1/2	0	1	
	(3)	1	0	1	
	(4)	3/2	-1	1	
	(5)	2	-1	1	
	(6)	4	-4	2	
$[M]_{\text{low}}$ $[MOH]_{\text{equilibrium}}$	(1)	1	-1	1	
	(2)	3/2	-1	1	
	(3)	2	-1	1	
	(4)	5/2	-2	1	
	(5)	3	-2	1	
	(6)	6	-6	2	

$$i = \bar{k}_{27}\bar{k}_{26}\bar{k}_{25}k_c[M]^0[OH^-]^{-2}[O_2] \exp(-5FE/RT) \quad (58)$$

The new mechanistic criteria are $\alpha = 5/2$, and reaction orders with respect to $[OH^-]$ and $[O_2]$ of -2 and 1 , respectively.

Substitution of Eq. (55) into Eq. (40) yields:

$$i = \bar{k}_{28}\{\bar{k}_{27}\bar{k}_{26}\bar{k}_{25}k_c[M]^0\}^{1/2}[OH^-]^{-3/2}[O_2]^{1/2} \times \exp(-2FE/RT) \quad (59)$$

These mechanistic criteria are $\alpha = 2$, and reaction orders with respect to $[OH^-]$ and $[O_2]$ of $-3/2$ and $1/2$, respectively.

If the coverage is considered to consist of chemisorbed oxygen atoms, then Eq. (54) determines the concentration of vacant sites. When the term $k_c[OH^-]^{-2} \times \exp(-2FE/RT)$ is much less than 1, as is the case for high coverage, Eq. (54) reduces to:

$$[M] = k_c[M]^0[OH^-]^{-2} \exp(-2FE/RT) \quad (60)$$

Eq. (60) could then be substituted into Eqs. (29), (32), (36) and (40) to yield new mechanism criteria in each case. However, this coverage condition will always lead to a reaction order with respect to $[OH^-]$ of at least -2 or a larger negative value. Such a value was never observed experimentally for oxygen reduction on the

Table 16
Path quoted by Ives and Janz [268]

(1) $M + O_2 + e^- \longrightarrow MO_2^-$	(2) $MO_2^- + H_2O \longrightarrow MO_2H + OH^-$	(3) $MO_2H + e^- \longrightarrow MO_2H^-$	(4) $MO_2H^- + H_2O \longrightarrow MO_2H_2 + OH^-$	(5) $MO_2H_2 + e^- \longrightarrow MOH + OH^-$	(6) $MOH + e^- \longrightarrow M + OH^-$
RDS no.	Calculated rate equations				
(1)	$i = k_1[M][O_2] \exp(-FE/2RT)$				
(2)	$i = k_2k_1[M][O_2] \exp(-FE/RT)$				
(3)	$i = k_3k_2k_1[M][OH^-]^{-1}[O_2] \exp(-3FE/2RT)$				
(4)	$i = k_4k_3k_2k_1[M][OH^-]^{-1}[O_2] \exp(-2FE/RT)$				
(5)	$i = k_5k_4k_3k_2k_1[M][OH^-]^{-2}[O_2] \exp(-5FE/2RT)$				
(6)	$i = k_6k_5k_4k_3k_2k_1[M][OH^-]^{-3}[O_2] \exp(-7FE/2RT)$				
Coverage conditions	RDS no.	α	$[OH^-]^m$	$[O_2]^p$	
$[M]_{\text{constant}}$ $[MOH]_{\text{equilibrium}}$	(1)	1/2	0	1	
	(2)	1	0	1	
	(3)	3/2	-1	1	
	(4)	2	-1	1	
	(5)	5/2	-2	1	
	(6)	7/2	-3	1	
$[M]_{\text{low}}$ $[MOH]_{\text{equilibrium}}$	(1)	3/2	-1	1	
	(2)	2	-1	1	
	(3)	5/2	-2	1	
	(4)	3	-2	1	
	(5)	7/2	-3	1	
	(6)	9/2	-4	1	

Table 17
Modified peroxide path 1

- (1) $M + O_2 + e^- \longrightarrow MO_2^-$
- (2) $MO_2^- + H_2O \longrightarrow MO_2H + OH^-$
- (3) $MO_2H + MH_2O + e^- \longrightarrow 2MOH + OH^-$
- (4) $MOH + e^- \longrightarrow M + OH^-$

RDS no. Calculated rate equations

- (1) $i = k_1[M][O_2] \exp(-FE/2RT)$
- (2) $i = k_2k_1[M][O_2] \exp(-FE/RT)$
- (3) $i = k_3k_2k_1[MH_2O][M][OH^-]^{-1}[O_2] \exp(-3FE/2RT)$
- (4) $i = k_4\{k_3k_2k_1[MH_2O][M]\}^{1/2}[OH^-]^{-1}[O_2]^{1/2} \exp(-3FE/2RT)$

Coverage conditions	RDS no.	α	$[OH^-]^m$	$[O_2]^p$
$[M]_{\text{constant}}$	(1)	1/2	0	1
	(2)	1	0	1
	(3)	3/2	-1	1
	(4)	3/2	-1	1/2
$[M]_{\text{low}}$	(1)	3/2	-1	1
	(2)	2	-1	1
	(3)	7/2	-3	1
	(4)	5/2	-2	1/2

Table 18
Modified peroxide path 2

(1) $M + O_2 + e^- \rightarrow MO_2^-$
 (2) $MH_2O + MO_2^- \rightarrow MOH + MO_2H^-$
 (3) $MO_2H^- \rightarrow MO + OH^-$
 (4) $MO + MH_2O \rightarrow 2MOH$
 (5) $MOH + e^- \rightarrow M + OH^-$

RDS Calculated rate equations no.

(1) $i = k_1[M][O_2] \exp(-FE/2RT)$
 (2) $i = k_2k_1[MH_2O][M][O_2] \exp(-FE/RT)$
 (3) $i = k_3k_5k_2k_1[MH_2O][OH^-]^{-1}[O_2] \exp(-2FE/RT)$
 (4) $i = k_4k_5k_3k_2k_1[MH_2O]^2[OH^-]^{-2}[O_2] \exp(-2FE/RT)$
 (5) $i = k_5\{k_4k_3k_2k_1[M][MH_2O]^2\}^{1/2}[OH^-]^{-1/2}[O_2]^{1/2} \exp(-5FE/6RT)$

Coverage conditions	RDS no.	α	$[OH^-]^m$	$[O_2]^p$
[M] _{constant}	(1)	1/2	0	1
	(2)	1	0	1
	(3)	2	-1	1
	(4)	2	-2	1
	(5)	5/6	-1/3	1/3
[M] _{low}	(1)	3/2	-1	1
	(2)	3	-2	1
	(3)	3	-2	1
	(4)	4	-4	1
	(5)	11/6	-4/3	1/3

polymer carbon electrodes tested. For this reason, the mechanisms are not analysed for the condition of potential-dependent coverage of surface sites by chemisorbed oxygen atoms, unless [M] occurs to the 1/2 power or less in the constant coverage rate equations.

The following Tables 1 to 18 analyse the mechanisms applicable to this study. The rate equation and resulting mechanistic criteria for each RDS assumption are tabulated under both the conditions of constant coverage and the potential-dependent coverage of the surface sites by chemisorbed hydroxyl groups. Langmuir conditions of adsorption are assumed. The following coverage Eqs. are used:

$$[M]_{low} = [M]^0 k_c [OH^-]^{-1} \exp(-FE/RT) \quad (61)$$

$$[MH_2O] = k_h [M] \quad (62)$$

$$[MOH]_{equil} = [M] k_c^{-1} [OH^-] \exp(FE/RT) \quad (63)$$

Further discussion of these mechanisms is reserved for a future publication.

Acknowledgement

The authors wish to express their thanks to JNICT, Portugal, for financial support (BD/899/90-RM).

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