TOWARDS FUEL CELL AND METAL-AIR BATTERY DEVELOPMENT – PART-1 THE MECHANISM OF OXYGEN REDUCTION AT LANTHANUM MANGANATE-BASED PEROVSKITE-TYPE OXIDES IN ALKALINE SOLUTION

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ABSTRACT

The electrocatalysis of oxygen reduction reaction by lanthanum strontium manganate ($La_{0.5}Sr_{0.5}MnO_3$) (LSM), lanthanum calcium manganate ($La_{0.5}Ca_{0.5}MnO_3$) (LCM) and lanthanum barium manganate ($La_{0.5}Ba_{0.5}MnO_3$) (LBM) has been studied by linear sweep cyclic voltammetry using rotating ring-disc electrode technique in alkaline medium. From the ring-disc data and other kinetic parameters it has been assumed that oxygen reduction occurs by dissociative chemisorption at low overpotentials. At higher overpotentials the formation of hydrogen peroxide has been observed on these electrocatalysts. The apparent exchange current density values for oxygen reduction on LSM, LCM and LBM have been found to be 2×10^{-7}, 5×10^{-8} and 4×10^{-8} $A.cm^{-2}$ respectively, while the corresponding Tafel slopes are 0.100, 0.115 and 0.115 V per decade. The possible reaction mechanism for electroreduction of oxygen on these oxide catalysts has been discussed.

Key words : Fuel cell, metal-air battery, lanthanum mangante, perovskite-type oxides, mechanism of oxygen reduction

INTRODUCTION

During the last decade interest has been shown by many researchers in development of newer electrode materials useful for the electrochemical reduction or evolution of oxygen, as oxygen electrocatalysis is of special importance to fuel cells, industrial water electrolysers and secondary metal-air batteries. Virtually all the catalysts of commercial importance are semiconductors. The conductivity of most transition metal oxides can be significantly improved by doping with suitable oxide whose cation is of lower valency than the cation of the host oxide. The perovskite-type oxides with good conductivity have become of interest because of these reasons. The advantage with these oxides is that oxygen ions are, in general, very mobile in this particular cubic ABO_3-type structure.

It has been shown by a number of researchers [1 & 2] that, of the different perovskite oxide systems studied for oxygen reduction in alkaline medium, lanthanum strontium manganate, $La_{1-x}Sr_xMnO_3$, exhibits better performance. The pervoskite-type oxides are reported [3] to reduce oxygen molecule to hydroxyl ion involving four electron transfer.

In this laboratory work has been in progress to find other lanthanum manganates which have either equal or better activity for the oxygen electrode reaction than the above said oxide. In this connection, an attempt has been made to replace strontium ion, Sr^{2+} whose ionic size (1.12 Å) is very much similar to that of lanthanum ions, La^{3+} (1.06 Å) by bivalent ions of slightly smaller and slightly bigger size to bring about a certain amount of distortion in the crystal structure without destroying the crystal structure as such, as this is assumed to have higher activity than the perfect structure. Calcium ion and barium ion whose ionic sizes are 0.99 Å and 1.34 Å respectively have been chosen for this purpose to prepare the oxides, namely, lanthanum calcium manganate $La_{0.5}Ca_{0.5}MnO_3$ and lanthanum barium manganate $La_{0.5}Ba_{0.5}MnO_3$. In the present paper the electrocatalytic behaviour of the lanthanum calcium manganate (LCM), and lanthanum barium manganate (LBM) has been studied and compared with that of lanthanum strontium manganate (LSM).

Oxygen reduction reaction has been studied by a number of workers [4] using rotating ring disc electrode technique for distinguishing the reaction paths on semiconducting mixed metal oxide and platinum group metal electrodes. Therefore, the present study was carried out adopting rotating ring-disc electrode technique (catalyst being coated on disc electrode) using slow sweep cyclic voltammetric method in alkaline medium.

EXPERIMENTAL

Materials

The method of preparation of the perovskite-type oxides LSM, LCM, and LBM is similar to that described in literature [1] using the respective oxides, which were obtained by the decomposition of their salts. These oxides were mixed thoroughly in a paste mortar by grinding well. They were then sintered at 1000°C for 48 hrs. The ABO_3 structure formation of the oxides after sintering was verified from x-ray diffractograms obtained. The specific resistances of the sintered oxides at a pressing pressure of 1.5 tons.cm^{-2} were found to be 1.2, 0.8 and 1.0 ohm.cm for LSM, LCM and LBM respectively. These values are fairly close to the reported value [1]. The whole system of the oxide has the cubic pervoskite structure. In the substitution of La^{3+} by Sr^{2+} or Ca^{2+} or Ba^{2+}, charge compensation is achieved simultaneously both by conversion of Mn^{3+} to Mn^{4+} and by formation of oxygen vacancies. The compositions in the system can be formulated for the oxides, in general, as:

$$La^{3+}_{(1-x)} (Sr^{2+}/Ca^{2+}/Ba^{2+})_x Mn^{3+}_{(1-x+2y)} Mn^{4+}_{(x-2y)} O^{2-}_{(3-y)} (Vo'')_y$$
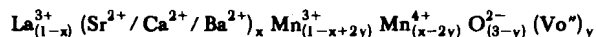
The electrochemical measurements have been carried out in an all-glass three-compartment cell. The catalyst powders were mixed with polystyrene binder, 10% by weight, in benzene and applied onto the gold-plated Pt-disc electrode. A cyanide bath was used for electroplating of gold on platinum disc electrode. The bright Pt ring was platinised. The electrolyte was prepared from GR grade KOH and thrice-distilled conductivity water. The electrolyte solution was pre-electrolysed for 48 hrs with purified nitrogen gas bubbling through the electrolyte solution using Ni-mesh electrodes, as platinum electrode has been reported to contaminate the solution [5]. The potentials were measured against Hg/HgO reference electrode.

Measurements

The details of the rotating ring-disc electrode (RRDE) assembly were given elsewhere [6]. A twin potentiostat, home made, similar to one described by earlier researchers [1] was employed for RRDE studies. Linear sweep cyclic

voltammograms for the disc and ring electrodes were recorded using Digilog x-y/t recorder of 2000 series. The rotation speed of the electrode was monitored using digital RPM counter. The HO_2^- intermediate formed at the disc electrode was quantitatively detected on platinized platinum ring electrode. The ring electrode was held at + 0.2 V where prior measurements indicated that HO_2^- oxidation is diffusion-controlled at this potential. A small ring current was observed at all potentials even in deaerated solutions. This background ring current was subtracted from the observed ring currents. The collection efficiency N for the disc-ring electrode system was calculated from the geometry of the ring-disc electrodes and found to be N = 0.58.

RESULTS AND DISCUSSION

In the oxides with the perovskite structure, oxygen ions are in general very mobile. From an electrochemical point of view, it will be of interest to know whether the oxide having very mobile oxygen ion in it keeps its original composition in the process of appreciable polarization at potentials corresponding to oxygen reduction. Therefore, surface characterization of lanthanum manganate oxides is of special importance in this regard before the electrocatalytic activity for oxygen reduction is studied in detail. Hence the stability of the oxide in alkaline medium has been evaluated using linear sweep cyclic voltammetric (LSCV) method. The catalyst coated on glassy carbon electrode (GCE) has been studied for its electrochemical behaviour in solutions deaerated with N_2 gas in the potential region of 0.1 V to −0.6 V and 0.8 V to −0.6 V, the results of which are shown in Fig. 1 (curves a, b & c).
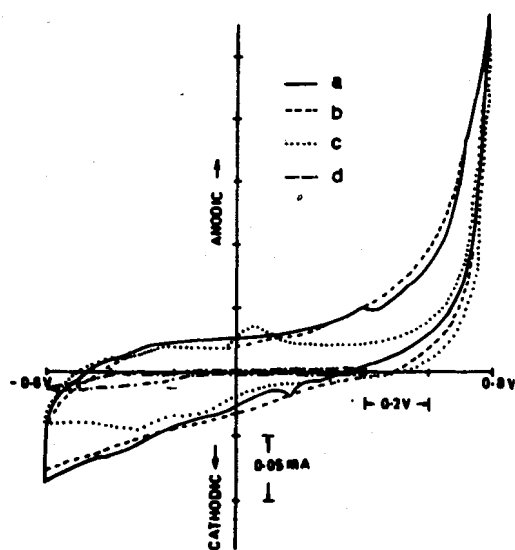

Fig. 1: Linear sweep cyclic voltammograms of LSM, LCM, LBM and GCE (curves a, b c and d respectively) in 1 M KOH solution deaerated with N_2 gas, at a sweep rate of 10 mV.sec.⁻¹

The voltammograms obtained for GCE without catalyst coating is shown in Fig. 1 d. The voltammograms show that in the cathodic region, the oxides are quite stable, unlike some of the systems which get reduced [1,8]. In the anodic potential region also, the catalysts maintain their stability and the evolution of oxygen is observed at a potential of about 0.6 V.

Rotating Ring-Disc studies

The disc and ring currents as a function of the disc potential for oxygen reduction on LSM, LCM and LBM in KOH solution at different speeds in the range of 470 to 2300 rotations per minute are shown in Figs. 2, 3 & 4. From these figures it is observed that the ring current, indicating the formation of HO_2^- at the disc electrode is negligible in the potential region up to about −0.2 V starting from the rest potentials of 0.1 V on all the three

perovskite oxide catalysts. Above this potential there appears a small ring current I_r which gradually increases as the disc potential is made more cathodic up to −0.6 V studied. The ring currents as well as the disc currents are dependent on rotation speed (ω) of the electrode.
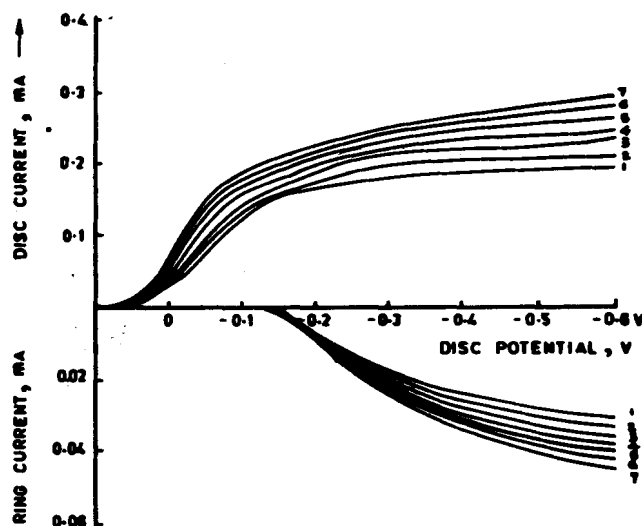

Fig. 2: Oxygen reduction currents at lanthanum strontium manganate disc and H_2O_2 oxidation currents at a Pt/Pt ring in 1 M KOH solution saturated with O_2 gas at different rotation speeds of (1) 470 (2) 670 (3) 950 (4) 1500 (5) 1670 (6) 1850 and (7) 2300; sweep rate is 10 mV.sec.⁻¹
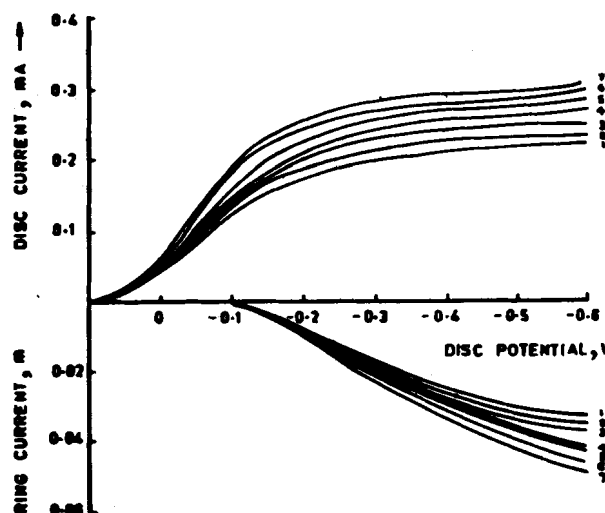

Fig. 3: Oxygen reduction currents at lanthanum calcium manganate disc and H_2O_2 oxidation currents at a Pt/Pt ring in 1 M KOH solution saturated with O_2 gas at different rotation speeds of (1) 470 (2) 670 (3) 950 (4) 1500 (5) 1670 (6) 1850 and (7) 2300; sweep rate is 10 mV.sec.⁻¹
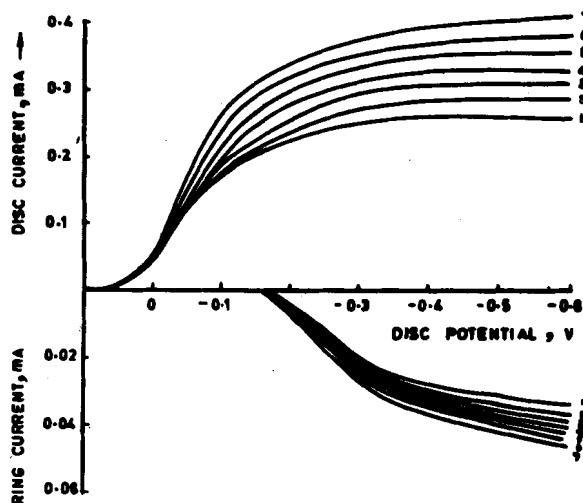
the slopes of the straight lines of the above figures. In the lower overpotential region, the curves have negative slopes. As the potential is increased, the curves slowly become horizontal and at higher overpotentials, the curves show positive slope for all the systems in general. In all the cases the value of intercept decreases with increase of overpotential. This indicates that in the lower overpotential region, the major reaction is that of the reduction of oxygen to hydroxyl ion without the formation of peroxide ion intermediate.
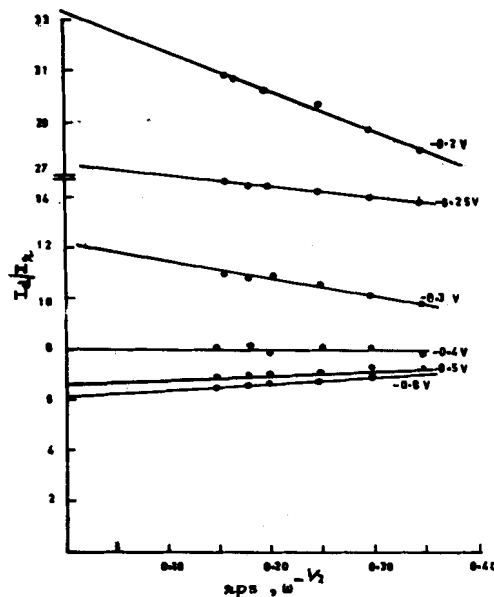

Fig. 4 : Oxygen reduction currents at lanthanum barium manganate disc and H₂O₂ oxidation currents at a Pt/Pt ring in 1 M KOH solution saturated with O₂ gas at different rotation speeds of (1) 470 (2) 670 (3) 950 (4) 1500 (5) 1670 (6) 1850 and (7) 2300; sweep rate is 10 mV.sec.⁻¹

It can be observed from these figures that the disc current is more for oxygen reducion reaction on LBM catalyst when compared with LSM or LCM whose disc currents I_d are of similar magnitude at any given potential and rotation speed. This indicates that LBM is a better electrocatalyst for oxygen reduction. Diffusion-limiting currents are observed above −0.5 V for all the three oxide catalysts which increase with an increase of rotation speed.

The plot of limiting disc current density as a function of $\omega^{-1/2}$, for LCM, LSM and LBM shows straight lines which pass through the origin (fig. not shown). The three straight lines exhibit different slopes.

The oxygen reduction reaction on the three perovskite oxides is a mixed controlled process i.e., controlled by both kinetic and diffusion up to a certain potential above which the process becomes more and more of diffusion controlled.

Plotting disc current values against rotation speed at different potentials and extrapolating them to f → ∞, makes the determination of the kinetic current $I_k = nFkC_{bulk}$ possible. These plots are linear but not parallel to each other which probably indicates that the oxygen reduction is not first order with respect to dissolved oxygen. The mass transfer corrected I_d are then used for plotting Tafel lines (figure not shown) for LCM, LSM and LBM electrocatalysts in 1 M KOH solution at 27° C. These plots show Tafel slopes of 100, 115 and 115 mV per decade for LSM, LCM and LBM respectively. Deviation from Tafel linearity begins at a potential of about −0.2 V for all the three systems. The corresponding exchange current density values are $2 \times 10^{-7}, 5 \times 10^{-8}$ and 4×10^{-8} A.cm⁻² for LSM, LCM and LBM respectively. The deviations from the Tafel lines are caused most likely by the occurrence of parallel sequential reaction as the potential where the deviation occurs corresponds to the beginning of ring current.

Plots of I_d / I_r vs $\omega^{-1/2}$ obtained from the experimental data of the present study for the three catalysts at various electrode potentials are shown in Figs. 5, 6 and 7. In these figures, plots have been drawn for the ring current values starting from the potentials above −0.2 V as, at potentials below this value, ring currents were not observed at. From the plots of I_d / I_r vs $\omega^{-1/2}$, it can be concluded that the reaction mechanism undergoes a change as the electrode potential is shifted towards the negative direction. This becomes obvious if one examines the potential dependence of the intercepts and of

Fig. 5 : Plots of (I_d/I_r) vs $\omega^{-1/2}$ obtained at various potentials in O₂−saturated 1 M KOH solution at a lanthanum strontium manganate electrode
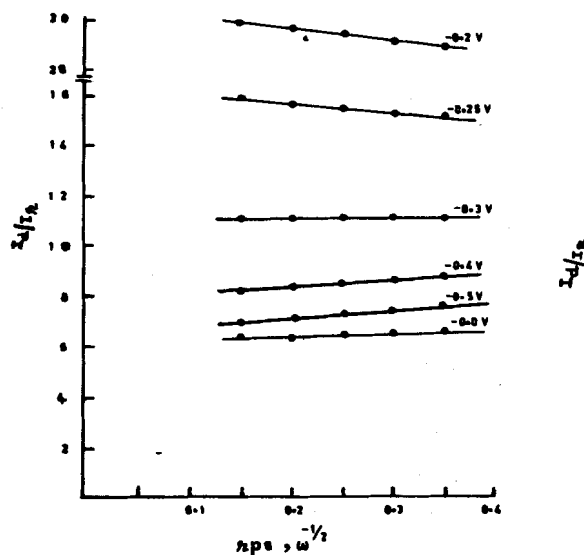

Fig. 6: Plots of (I_d/I_r) vs $\omega^{-1/2}$ obtained at various potentials in O₂−saturated 1 M KOH solution at a lanthanum calcium manganate electrode
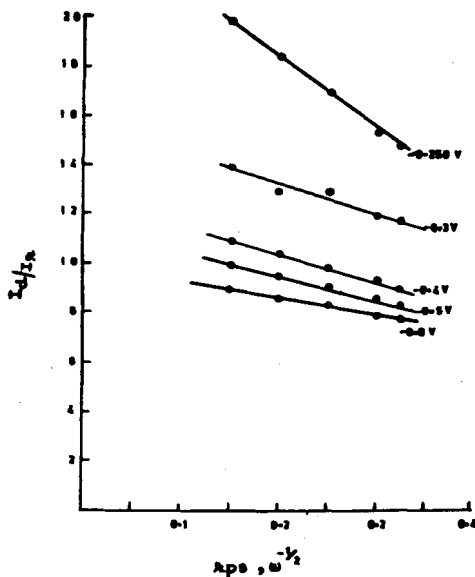
Fig. 7 : Plots of (I_d/I_r) vs $\omega^{-1/2}$ obtained at various potentials in O_2—saturated 1M KOH solution at a lanthanum barium manganate electrode

Several models have been proposed to explain the mechanism of the O_2 reduction reaction using rotating ring disc electrode technique. A criterion has been proposed [9] to distinguish two possible reaction mechanisms of O_2 reduction from the plot of the ratio I_d to I_r currents vs the reciprocal of the square root of the electrode rotating speed (ω). The first mechanism is a direct reduction path which reduces O_2 to OH^- through a four electron step. The second mechanism is a series reaction path where oxygen is first reduced to HO_2^- followed by the reduction of HO_2^- to OH^-. The adsorption-desorption step of HO_2^- at the disc has been taken into consideration by some researchers [10]. Later the theory was extended [11] to porous elelctrodes to include the catalytic decomposition of HO_2^- to O_2 and OH^- In another reaction model proposed [5] for O_2 reduction on gold in alkaline solution only the series reaction path was considered. Literature survey indicates that a simple reaction model [9] is consistent with many of the reported experimental results. But in view of the present RRDE data in which one observes that the end product depends on the applied potential, it has been assumed that HO_2^- ion maintains an adsorption-desorption equilibrium and this equilibrium constant is dependent on the potential of the electrode. The reaction model can be written as:

Here k_1 represents the direct reduction to OH^- ion i.e. without the formation of an intermediate that can be desorbed and detected on the ring of a rotating ring disc electrode experiment; k_1 will describe equally well any reaction in which the reductive splitting of the O-O bond occurs entirely in the adsorbed state, and the RRDE diagnostic criteria will not allow a distinction to be made between an electrochemical reductive cleavage and dissociative chemisorption of oxygen molecule. The routes shown in the above scheme are therefore relative to the possibilities offered by the RRDE method, and although this may appear to be a limitation, its usefulness has been repeatedly demonstrated. The factor k_2 is an overall rate constant for the formation of adsorbed peroxide, and may involve other rate constants that are related to both the intermediate formation of adsorbed super oxide and its disproportionation reaction; k_3 is the rate constant for reduction of peroxide, k_4 refers to the dismutation of adsorbed peroxide, and k_5 and k_6 represent rate constants for the process of desorption and adsorption of peroxide.

It has also been shown[9] that the expression for the calculation of rate constants may be written as:

$$\frac{I_d}{I_r} = \frac{1 + 2 k_1 / k_2}{N} + \frac{2(1 + k_1 / k_2)}{N_2} k_3 \, \omega^{-1/2} \qquad (1)$$
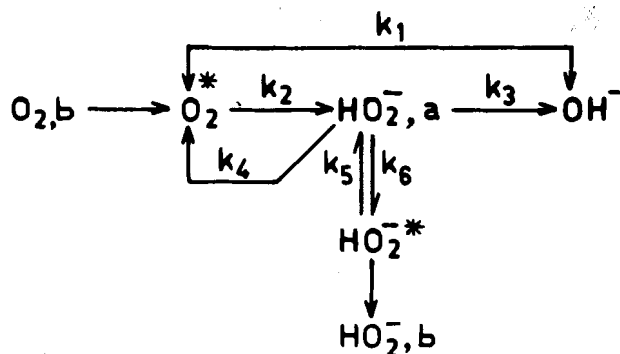
which can be modified as:

$$\left[\frac{I_d}{I_r} \right]_{\omega^{-1/2} \to 0} = \frac{1 + x}{N} \qquad (2)$$

where $x = \dfrac{2 k_1}{k_2}$

From the present experimental results of RRDE, it has been calculated that the value of x becomes 10 and above, at a potential of about -0.2 V for the three oxide catalysts which is the value for the ratio of the partial current at the disc electrode due to the reduction of oxygen to OH^- ion, and partial current at the same electrode due to reduction to HO_2^-. As the potential is made more and more cathodic, current for oxygen reduction to HO_2^- increases comparatively. As the slopes of the lines increases with increasing electrode potentials, it follows that k_3 increases with increasing potential, and hence at these potentials, peroxide ion intermediate reduces further to hydroxyl ion at a rate that increases with increasing overpotential. But even at these potentials the value of k_1 does not become zero. At the intermediate potentials where the slope is nearly zero, the rate constant k_3 for the reduction of peroxide ion is small. Peroxide ion formed at these potentials is not further reduced to hydroxyl ion at a rate comparable with that by which it is produced.

Accordingly we can conclude that the main reaction at lower overpotential region is O_2 reduction to OH^- ion directly, but as the potential is made cathodic, gradually O_2 reduction to HO_2^- begins which reduces slowly to OH^- ion and at still higher cathodic potentials reduction to OH^- ion through the formation of HO_2^- intermediate takes place at comparatively higher rates.

Effect of Oxygen Partial Pressure

The 'pseudo spilitting' theory predicts that for every molecule of oxygen chemisorbed 'side-on', there will be two electron-transfer centres. Thus the rate of oxygen chemisorption should be directly proportional to the square root of oxygen partial pressure. To verify this and to determine the value of n in the general relation $I = kp^n$, oxygen reduction on RDE (of RRDE) has been studied at different partial pressures of oxygen, by diluting it with nitrogen, and at a constant rotation speed of 2300 rpm. After correcting for the residual current, log I vs log P_{O_2} plots have been drawn at different potentials in the range of -0.05 to -0.25 V for all the three perovskite oxide systems (figure not shown). The slopes for the three catalysts have been observed to be in the range 0.45 $-$ 0.55, up to a potential of about -0.15 V, and above this potential the value was found to increase with increase of overpotentials. This value indicates that dissociative chemisorption of oxygen molecule

takes place in this low overpotential region on the surface of the catalysts. Similar type of observations have been reported [3,12] for the oxide catalysts for oxygen reduction reaction.

Effect of OH⁻ ion concentration

Oxygen reduction reaction on all the three perovskite catalysts has been studied using RDE in different concentrations of OH⁻ ions, at a constant rotation of 2300 rpm. The results obtained show that the rate is not appreciably affected by variation in the concentration of OH⁻ ion for the three electrocatalysts.

Discussion of reaction mechanism

The Tafel slope for all the three oxide catalysts amount to about 100-115 mV decade⁻¹. It has been suggested [13] that the rate determining step is the transfer of the first electron:

$$O_2 + e \rightarrow O_2^- \text{ (alkaline)} \quad (3)$$

This step satisfies the observed independence of OH⁻ ion concentration on rate but the effect of partial pressure of O_2 is not fulfilled which can best be explained by considering the dissociative chemisorption of oxygen molecule on the surface of the electrode prior to rate determining first-electron transfer step i.e.

$$O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2O_{(ads)} \quad (4)$$

$$O_{(ads)} + e \overset{k_2}{\longrightarrow} O^- \quad (5)$$
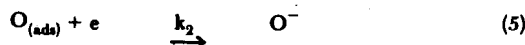
Assume p to be the partial pressure of O_2 in contact with the electrode and θ to be the fraction of energetically the geometrically suitable sites covered by chemisorbed dissociated oxygen at a given current 'I'. Considering quasi-steady state and taking into account that the adsorption follows Langmuir as the surface coverage by oxygen is low [12] the rate equation can be written as:

$$V - k_2 \; \theta_{ads} \exp \left[\beta \; \frac{vF}{RT} \right] \quad (6)$$

substituting the value of θ_{ads} from the above reaction one gets

$$V - k_2.k.(1 - \theta_{ads})^{1/2} \; PO_2^{1/2} \exp \left[\beta \; \frac{VF}{RT} \right] \quad (7)$$

The above rate expression satisfies the observed kinetic parameters at low overpotentials. But at high potentials, because of formation of HO_2^- species at the disc electrode as is evidenced by the ring current, the reaction mechanism changes from direct reduction of O_2 molecule to OH⁻ ion without undergoing intermediate formation of HO_2^- to parallel mechanism with the formation of HO_2^- ion as an intermediate.

For an interpretation of the results, some of the general features of the possible reaction mechanism have been considered as shown in Fig. 8 [14]. Oxygen reduction in aqueous solutions requires a strong interaction of oxygen molecule with the electrode surface for the reaction to proceed at a reasonable rate. Three types of models for such an interaction have been proposed [14]. The Griffith's model has assumed a lateral interaction of the π — orbitals of the O_2 with empty dz^2 orbitals of a transition element, ion or metal atom with back bonding from at least partially filled d_{xy} or d_{yz} orbitals of the transition element to the π^* orbitals of the O_2 molecule. This type of interaction leads to a weakening of the O-O bond with corresponding lengthening of this bond. In the Pauling model the Sp^2 orbitals of O_2 interact with dz^2 orbitals of the transition metal. This adsorption of O_2 is expected to be accompanied by at least a partial charge transfer to yield a super oxide and then peroxide state. The bridge model provides an alternate means for bringing about rupture of the O-O bond through the formation of −O-O-bridge. The formation of bridge species also requires that the two metal species have partially filled d_{xy} or d_{yz} orbitals to participate in bonding with the Sp^2 orbitals of the oxygen.

From the above models it can be concluded that the end-on adsorption

(Pauling model) of O_2 mainly leads to HO_2^- formation in alkaline solutions. Side-on adsorption which probably is responsible for dissociative adsorption (Griffith's model and Bridge model) implies a weakening of the O-O bond and a direct reduction of O_2 to OH⁻ ion.
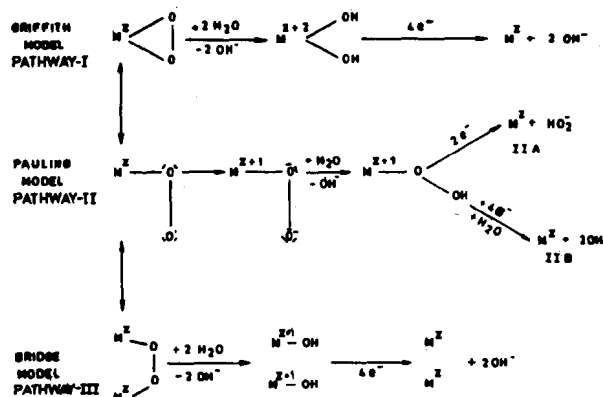

Fig. 8: Models for O_2 adsorption at electrodes and subsequent pathways of O_2 reduction in alkaline solution

The rotating ring disc results and kinetic parameters observed for oxygen reduction reaction on the three oxide catalysts cannot be explained completely by considering any of the three models mentioned above. The zero ring current and the effect of partial pressure of O_2 on the rate at low overpotentials can be explained by considering either Griffith's model or Bridge model. To distinguish the possible adsorption of oxygen from these two models one may have to consider the interatomic distance of the transition metal ions of dual valencies. As the atoms of oxygen molecule can possibly adsorb on the two different valence ions, the bridge model appears probable in the case of perovskites. The dissociative side on adsorption of oxygen molecule on the transition metal ions of the perovskite structure has been postulated by some researchers [15].

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