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Oxygen Reduction at a Manganate Electrocatalyst in KOH Solutions

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A eletrocatálise da reação de redução do oxigênio por manganato de cálcio e lantânio, ($La_{0.5}Ca_{0.5}MnO_3$) (LCM), foi estudada por voltametria cíclica usando-se a técnica do eletrodo rotativo de disco e anel (RRDE) em meio alcalino. Os resultados do disco-anel e outros parâmetros cinéticos indicaram que, a baixas sobretensões, a redução do oxigênio ocorre por adsorção química. Para sobretensões mais elevadas foi observada a formação de peróxido de hidrogênio (HO_2^- neste caso) no eletrocatalisador. A densidade de corrente de permuta aparente, determinada para a redução do oxigênio no LCM foi de 5×10^{-8} A cm^{-2}, sendo o correspondente coeficiente de Tafel de 0,115 V por década. Discute-se e sugere-se um mecanismo para a reação de eletro-redução do oxigênio.

The electrocatalysis of the oxygen reduction reaction by lanthanum calcium manganate, ($La_{0.5}Ca_{0.5}MnO_3$) (LCM) has been studied by cyclic voltammetry using the rotating ring-disc electrode technique (RRDE) in alkaline medium. From the ring-disc data and other kinetic parameters it has been assumed that the oxygen reduction occurs by dissociative chemisorption at low overpotentials. At higher overpotentials, the formation of hydrogen peroxide (HO_2^- in this case) has been observed on this electrocatalyst. The apparent exchange current density value for oxygen reduction on LCM has been found to be 5×10^{-8} A cm^{-2}, while the corresponding Tafel slope is 0.115 V *per* decade. The possible reaction mechanism for electroreduction of oxygen on this oxide catalyst has been discussed.

Keywords: fuel cell, metal-air battery, lanthanum calcium manganate, oxygen reduction, HO_2^- disproportionation

Introduction

Fuel cells and metal-air batteries are energy generators that hold considerable potential for future application and relatively clean generation of electricity. These electrochemical devices transform fuel energy into electricity without the need for a thermal cycle. One of the major concerns of fuel cells research is the development of good electrocatalysts for the oxygen reduction reaction. Platinum group metal electrodes,[1,2] activated carbons,[2,3] semiconducting mixed metal oxides,[4] among others,[5,6] are a family of materials that have been shown to possess good catalytic activity for oxygen reduction at low temperature.

Manganese oxides and other metal Mn-containing oxides are well known as thermally stable catalysts in many industrial and environmental applications, and have been reported to effect a four electron-reduction of O_2 to OH^-.[2,7,8]

In the present paper, the electrocatalysis of the oxygen reduction reaction by lanthanum calcium manganate, $La_{0.5}Ca_{0.5}MnO_3$ (LCM) has been studied by linear sweep cyclic voltammetry (LSCV) using the rotating ring-disc electrode technique (RRDE) in KOH solutions.

Experimental

The method of preparation of the LCM was similar to that described in the literature[9] using La, Ca and Mn oxides obtained by the decomposition of their salts. These oxides were mixed and sintered at 1000 ºC, showing a specific resistance of 1.2 ohm cm at 1.5 ton cm^{-2}. Their composition could be formulated as $La^{3+}_{(1-x)}Ca^{2+}_{X}Mn^{3+}_{(1-x\,+\,2y)}O^{2-}_{(3-y)}(V_{O''})_y$ where ($V_{O''}$) are the oxygen vacancies required for charge compensation. The electrochemical measurements have

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been carried out with PAR equipment and a conventional three-compartment cell. The catalyst was coated onto the gold-plated Pt-disc electrode, and the bright Pt ring was platinised. The electrolyte was prepared from KOH (analytical grade) and bidistilled water, and the potentials were measured against a Hg/HgO reference electrode. The collection efficiency, N, for the RRDE system was calculated from the geometry of the ring-disc electrodes and found to be N ≅ 0.58.[9] The ring electrode was held at +0.2 V where prior measurements indicated that HO_2^- oxidation is diffusion-controlled at this potential.

Results and Discussion

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. Figure 1 shows two voltammograms for the coated (curve a) and uncoated (curve b) GCE electrode in the potential range of 0.8 V to -0.6 V.

The single and multiple CV measurements performed in the potential range of 0.1 V to -0.6 V showed that in the cathodic region, the catalyst is quite stable, unlike some of the systems which get reduced.[2,10] In the anodic potential region also, the catalyst maintains its stability and the evolution of oxygen is observed at a potential of about 0.6 V (measurements in the potential range of 0.8 V to -0.6 V, as it is shown in Figure 1, curve a).

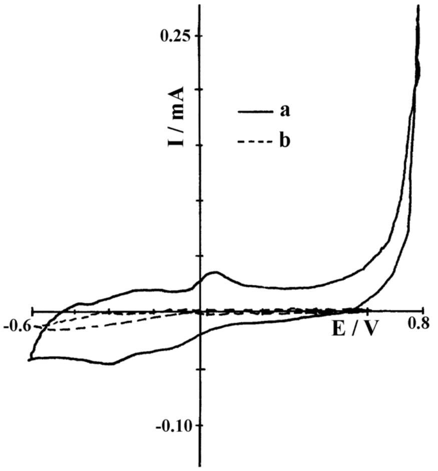

Figure 1. Linear sweep cyclic voltammograms of LCM and GCE (curves a, b, respectively) in 1mol L^{-1} KOH solution deaerated with N_2 gas, at a sweep rate of 10 mV s^{-1}.

The disc and ring currents as a function of the disc potential for oxygen reduction on LCM in KOH solution at different speeds in the range of 470 to 2300 rotations *per* minute are shown in Figure 2. It should be noted that a very small ring current was always observed at all disc potentials even in deaerated solutions. This background ring current was subtracted from the observed ring currents that correspond to the oxidation of the HO_2^- produced at the disk electrode during O_2 reduction.

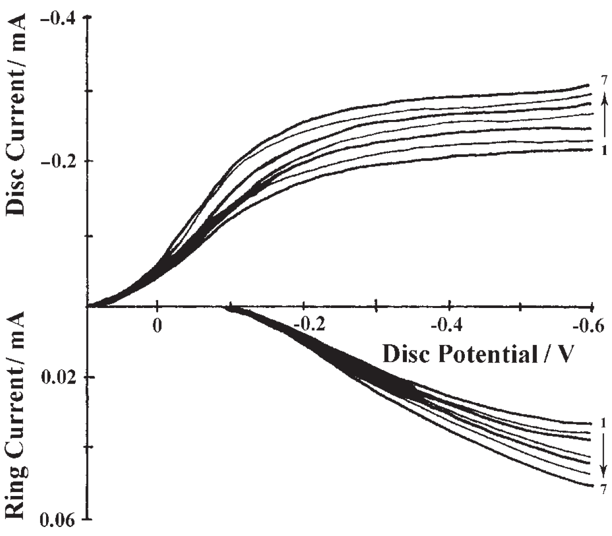

Figure 2. O_2 reduction currents at LCM disc and HO_2^- oxidation currents at a Pt/Pt ring in 1 mol L^{-1} KOH solution saturated with O_2 gas at different rotation speeds (rpm) of (1) 470, (2) 670, (3) 950, (4) 1500, (5) 1670, (6) 1850 and (7) 2300. Sweep rate: 10 mV s^{-1}.

From Figure 2, 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 potential of 0.1 V on the oxide catalyst. Above this potential there appears a small ring current I_r, which gradually increases as the disc potential is made more cathodic up to the -0.6 V studied. The ring currents as well as the disc currents are dependent on rotation speed (ω) of the electrode.

Plotting the limiting disc current as a function of $\omega^{1/2}$ for the electrocatalyst it is obtained a straight line with an intercept not equal to zero, as displayed in Figure 3. This Levich plot is in agreement with the curves shown in Figure 2, which do not show a well-defined plateau region only for the diffusion-limited processes. Koutecky-Levich plots at different disk potentials confirmed the previous conclusions, straight lines with distinct values of slope and intercepts different from zero being obtained.

The oxygen reduction reaction on the LCM oxide 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 diffusion controlled.

Plotting disc current values against rotation speed at different potentials and extrapolating them to $f \rightarrow \infty$ makes

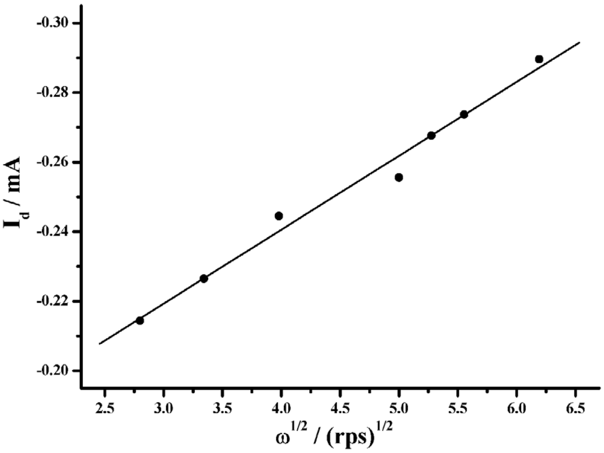

Figure 3. Levich plot for oxygen reduction at LCM in O_2-saturated 1mol L^{-1} KOH (ω in rotations *per* second).

the determination of the kinetic current $I_k = nFkC_{bulk}$ possible. Here k and C_{bulk} are the overall rate constant and oxygen concentration in the solution, respectively. 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. Plotting the Tafel line for the LCM electrocatalyst in 1 mol L^{-1} KOH solution at 27 ºC, a Tafel slope of 0.115 V *per* decade is obtained (Figure 4). I_d data used for these plots were corrected from mass transfer interference using the procedure described by Gojkovic *et al.*[11] Deviation from Tafel linearity begins at a potential of about -0.2 V for the LCM system. The corresponding exchange current density value is 5 x 10^{-8} A cm^{-2}.

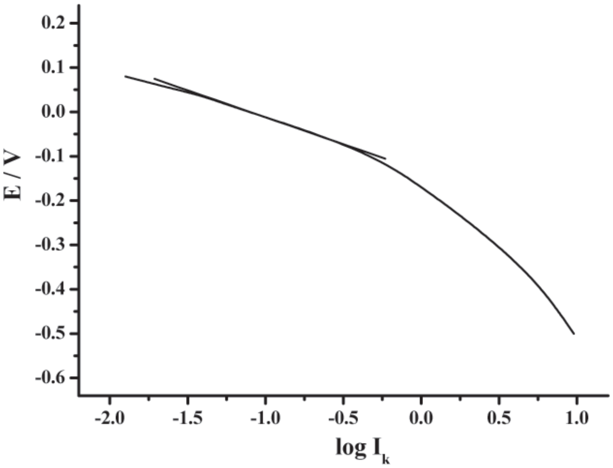

Figure 4. Mass-transfer corrected Tafel plot for the data obtained from the polarisation curves (Figure 2) for O_2 electroreduction in 1mol L^{-1} KOH at 27 ºC.

The deviations from the Tafel lines are caused most likely by the occurrence of parallel sequential reactions 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 LCM catalyst at various electrode potentials have been drawn (Figure 5).

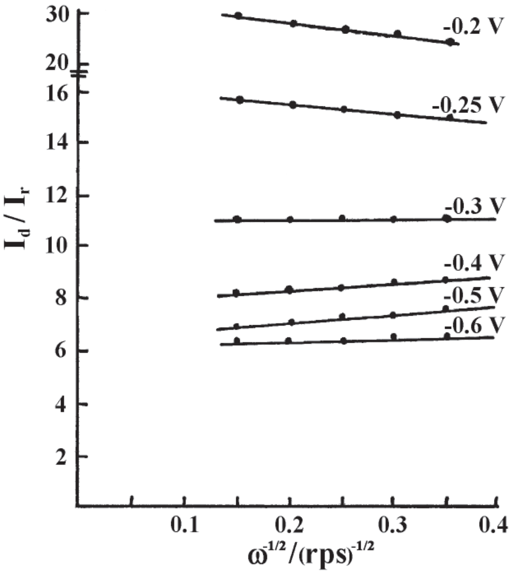

Figure 5. Plots of I_d/I_r *vs.* $\omega^{-1/2}$ obtained at various potentials in O_2-saturated 1 mol L^{-1} KOH solution at a LCM electrode (ω in rotations *per* second).

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 the slopes of the obtained straight lines. 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 slopes. 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.

Literature survey indicates that a simple reaction model[12] 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 may be dependent on the potential of the electrode. The reaction model can be written as shown in Figure 6.

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

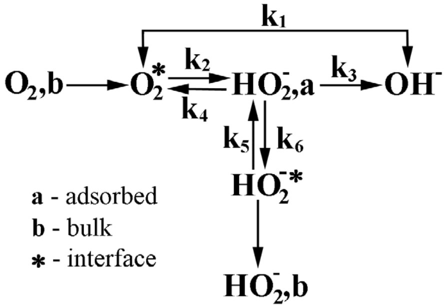

Figure 6. Suggested model for O_2 reduction in KOH solution.

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 the 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.

The main processes can be expressed as follows:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \qquad (1)$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \qquad (2)$$

$$2HO_2^- \rightarrow O_2 + 2OH^- \qquad (3)$$

it is being clear that the occurrence of the disproportionation reaction (3) may enhance the electrocatalytic activity of LCM effecting the four-electron reduction of O_2 to OH^-:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4)$$

as it has been shown by Mao *et al.*[8] for other manganese oxide electrodes.

It has also been shown[12] that the expression for the calculation of rate constants may be written as:

$$\frac{I_d}{I_r} = \frac{1+2k_1/k_2}{N} + \frac{2(1+k_1/k_2)}{N_2} k_3\, \omega^{-1/2} \qquad (5)$$

which can be modified as:

$$I_d/I_r = (1+x)/N \qquad (6)$$

when $\omega^{-1/2} \rightarrow 0$. Here, $x = 2k_1/k_2$.

From the present experimental results of RRDE, it has been calculated that the value of x becomes higher than 10, at a potential of about -0.2 V for the oxide catalyst 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 disc potential is made more and more cathodic, current for oxygen reduction to HO_2^- increases comparatively. As the slopes of the lines increase 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 more cathodic, O_2 reduction to HO_2^- gradually begins, which reduces slowly to OH^- ion. At still higher cathodic potentials, the reduction to OH^- ion through the formation of HO_2^- intermediate takes place at comparatively higher rates.

The "pseudo" splitting 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 $I_d = kp^n$, oxygen reduction on the disc electrode of the 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_d *vs.* log p_{O_2} plots have been drawn at different potentials in the range of -0.05 to -0.25 V for the oxide system. The slopes have been observed in the range 0.45-0.55, up to a potential of about -0.15 V, and above this potential the slope was found to increase with increase of overpotentials. This higher slope indicates that, in the low overpotential region, dissociative chemisorption of oxygen molecule takes place on the surface of the catalyst. Similar type of observations have been reported[13,14] for the oxide catalysts for oxygen reduction reaction.

The RRDE results and kinetic parameters observed for the O_2 reduction on the studied catalyst cannot be explained by considering the conventional models mentioned for these systems.[15-18]

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.[18] 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 our oxide catalyst. The dissociative side on adsorption of oxygen molecule on the transition metal ions of the LCM structure has been postulated by some researchers.[19]

Acknowledgments

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