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The Mechanism of Oxygen Reduction at a $LaNiO_3$ Electrode

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The reaction mechanism of the O_2 reduction at $LaNiO_3$ was studied by using a rotating ring-disc electrode, which consists of a $LaNiO_3$ disc and Pt ring electrodes. It was found that the O_2 was completely reduced to OH^- on the Hoare path. Oxygen vacancies seem to be required in the oxide surface for reduction of adsorbed O_2H^- to OH^-.

It was shown in previous studies[1,2] of the catalytic activity of transition metal oxides for the O_2 reduction that the band structure of oxides is a major factor in determining their catalytic activities. In order for the oxides to have a high catalytic activity, they must have a filled or partially filled σ^* band. $LaNiO_3$ satisfies this requisite, and hence shows high electrocatalytic activity for the O_2 reduction. It was also found that the O_2 reduction at $LaNiO_3$ and related oxides proceeded with the Hoare path and that the rate-determining electron transfer step, $O_2H+e \rightarrow O_2H^-$, was greately affected by the d-electron configuration in the σ^* band.

It is important to clarify the over-all reaction mechanism in order to elucidate the electrocatalysis of O_2 reduction. Especially important is the role which O_2H^- plays in the sequence of the reaction. The use of the rotating ring-disc electrode has been shown to be successful for this purpose.[3-7]

In the present study, therefore, the reaction mechanism of the O_2 reduction at $LaNiO_3$ is determined by using the rotating ring-disc electrode assembly, and the major factor which leads to O_2H^- formation is discussed.

Experimental

A rotating $LaNiO_3$ disc electrode with a Pt ring was prepared by the following method. A $LaNiO_3$ disc electrode of 6 mm diameter was prepared in the same manner as described in a previous paper,[8] and then assembled in a Teflon rod together with a Pt ring (6.7 mm in inner diameter and 9 mm in outer diameter). The area of the disc electrode was then 0.28 cm^2, and the geometric factor N was 0.39, as calculated from the dimension of the disc and ring electrodes.

The ring-disc electrode was set in a rotating ring-disc measurement system (Nikko Keisoku, model RRDE-1). The electrolytes were 1 M** NaOH and NaOH-Na_2SO_4 mixtures. The latter was prepared so as to give the same ionic strength as 2 M NaOH, but various pH values. A hydrogen electrode, H.E., in the test electrolytes was used as a reference electrode. The electrode potentials cited in this paper are referred to this electrode, unless otherwise stated.

As the pretreatment of the disc electrode, it was washed with acetone, followed by immersion in 0.5 M H_2SO_4 for 10 s, and then washed with distilled water.[9] The pretreatment of the Pt ring electrode was made electrochemically; it was polarized at 1.8 V for 30 s in the same solution as the test electrolyte in order to eliminate the adsorbed impurities on the surface, then at -0.1 V for 30 s to reduce an oxidized surface, and finally for about 3 h at 1.4 V, which was the same potential as that selected for detection of O_2H^-. The background current decreased to less than 0.2 μA by the final treatment, and thereby reproducible results could be obtained. Potential-current curves of the disc electrode were measured under a potentiostatic condition, and the oxidation current of O_2H^- at the ring electrode was measured at 1.4 V.[3]

Results

Figure 1 shows the ring current, I_r, and the disc current, I_d, as a function of disc electrode potentials, E_d. The rotation rate, ω, was set at 2000 min^{-1}. A very small ring current was observed in the potential region less positive than 0.825 V.

$1/J$ *vs.* $\omega^{-1/2}$ plots are shown in Fig. 2 for the limiting current region, where $J=|I_d|+I_r/N$. As shown in Fig. 1, I_r was very small compared with I_d, and hence I_r negligibly contributed to J. The conclusion can be drawn, therefore, from the good linearities between J and $\omega^{-1/2}$ that the reaction order of O_2 is 1[10] in the potentials giving a saturated $|I_d|$ at which the rate detremining step is O_2 adsorption to the electrode surface[1].

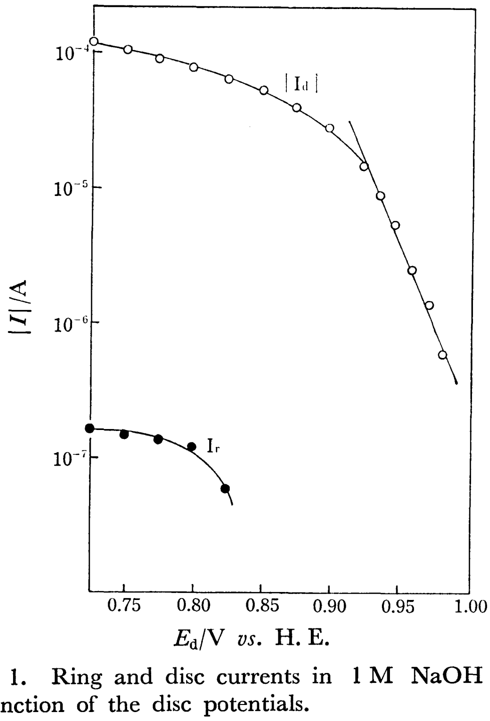


Fig. 1. Ring and disc currents in 1 M NaOH as a function of the disc potentials.

** M=mol·dm^{-3}.

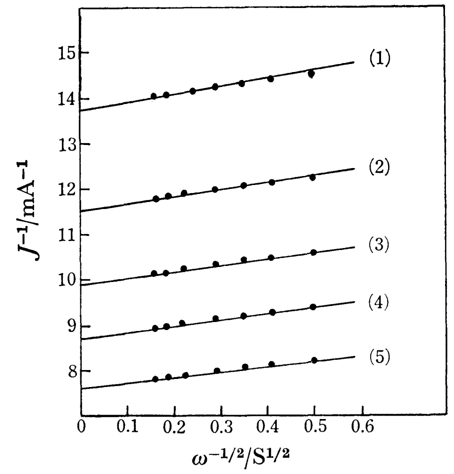


Fig. 2. $1/J$ *vs.* $\omega^{-1/2}$ plots in 1 M NaOH. E_d/V: (1) 0.825; (2) 0.8; (3) 0.775; (4) 0.75; (5) 0.725 (*vs.* H. E.).

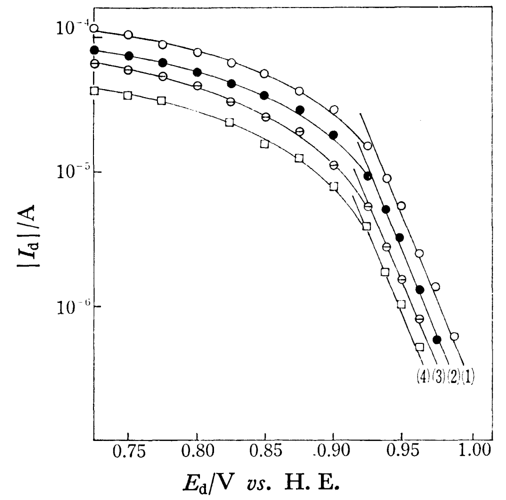


Fig. 3. Dependence of current-potential curve of O_2 reduction in 1 M NaOH on P_{O_2} at $\omega = 2000$ min^{-1}. P_{O_2}/atm: (1) 1; (2) 0.5; (3) 0.2; (4) 0.1.

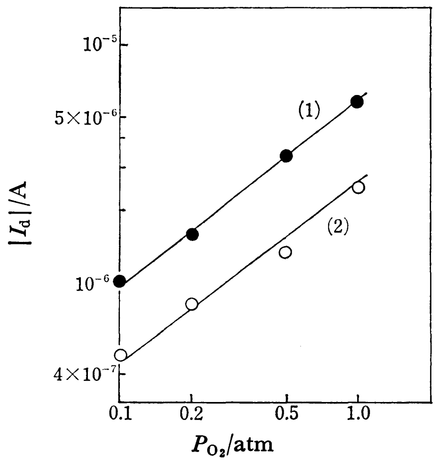


Fig. 4. log $|I_d|$ *vs*, log P_{O_2} plots in 1 M NaOH. E_d/V: (1) 0.95; (2) 0.9625 (*vs.* H. E.).

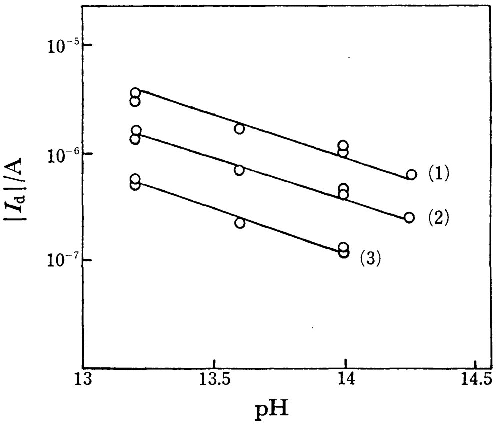


Fig. 5. log $|I_d|$ *vs.* pH plots in the Tafel region at $\omega = 2000$ min^{-1}. E_d/V: (1) 1.2; (2) 1.45; (3) 1.7 (*vs.* NHE).

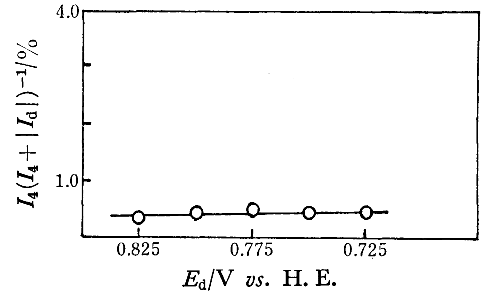


Fig. 6. $I_4/(I_4+|I_d|)$ at $\omega = 2000$ min^{-1} in 1 M NaOH as a function of the disc potentials.

Figure 3 shows an effect of introduced oxygen pressure, P_{O_2}, on the current-potential curves at the disc electrode. The relations between log P_{O_2} and log $|I_d|$ in the potentials giving the Tafel slope are shown in Fig. 4. The slope of the line in this figure is about 0.8, from which it is suggested that the reaction order of O_2 in the Tafel region is also 1.

Figure 5 shows $|I_d|$ in the Tafel region as a function of pH of the electrolytes. In this case, the disc potential values are converted into the normal hydrogen electrode scales so that the reaction order of OH^- can be directly obtained form the slope of log $|I_d|$ *vs.* pH plots.[11] It is noticed that good linearities were established between log $|I_d|$ and pH, and that the slope was about −0.8, although the points are a little scattered. This result implies that the reaction order of OH^- in this potential region is −1. Then the rate equation in the Tafel region can be written as follows with the rate constant k:

$$I_d = k[O_2][OH^-]^{-1}\exp(-\Delta G^*/RT), \qquad (1)$$

where ΔG^* is the electrochemical activation energy, which was discussed in detail in Ref. 12. Equation 1 contains all the reaction steps preceeding to the rate determining step.

Figure 6 shows $I_4/(I_4+|I_d|)$ as a function of the disc potentials, where I_4 denotes the total current of OH^- diffusing away from the disc electrode to the solution (Fig. 7), and is given by I_r/N.[13] The I_1 path in Fig.7 means that O_2 is directly reduced to OH^- through a side-on type adsorption of O_2. The value of $I_4/(I_4+|I_d|)$ was 0.4% and almost equal to those observed at cobalt mixed oxides ($CoO+Co_2O_3$), Co_3O_4, and Co_2NiO_4 electrodes,[6,7] suggesting that

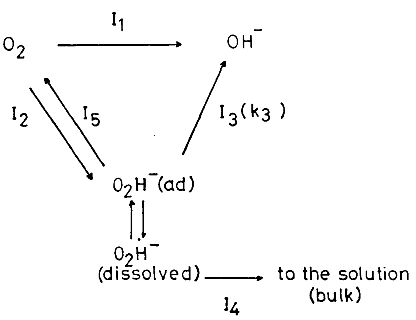


Fig. 7. A general scheme of O_2 reduction in alkaline solutions.

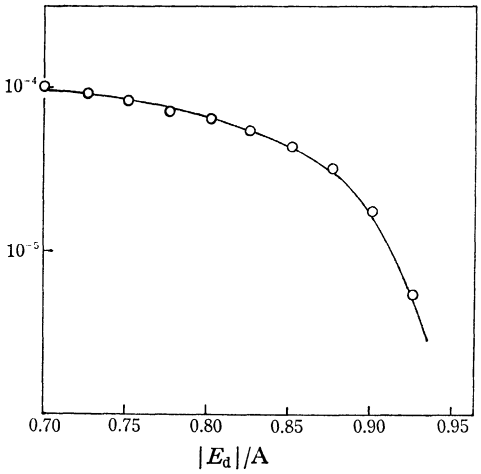


Fig. 8. Current-potential curves for reduction of O_2H^- at $\omega = 2000\ \text{min}^{-1}$.

O_2 is predominatnly reduced to OH^- at a $LaNiO_3$ electrode. The $|I_d|/I_r$ *vs.* $\omega^{-1/2}$ plots were so scattered that k_3 could not be determined. The small ring current seems to be responsible for the large scatter of the plots. In order to elucidate the role of OH^- in the reaction scheme of the Hoare path, the feasibility of the O_2H^- reduction was investigated in 1 M NaOH saturated with N_2. The O_2H^- concentration was 10^{-2} M. It was found that the reduction of O_2H^- proceeded easily at the disc electrode, as shown in Fig. 8.

As reported in a previous paper,[14] the NiO used as a starting material to synthesize $LaNiO_3$ remained as an isolated phase in $LaNiO_3$ if the preparation was made in a very short time or at a low temperature. Therefore, there is a possibility that the $LaNiO_3$ used in the present study contained a very small amount of isolated NiO, even though $LaNiO_3$ was prepared at 850 °C for 2 days. Bagotzky *et al.*[7] reported that O_2H^- ions were produced in the O_2 reduction on NiO at a potential region less positive than about 0.8 V and that the O_2H^- produced was not further reduced. This potential was in accord with that found in the present study for commencement of the very small ring current (see Fig. 1). Therefore, it seems reasonable to consider that NiO as an impurity in $LaNiO_3$ is responsible for the production of O_2H^- at the disc electrode. If this view is valid, then it can be concluded that O_2 is completely reduced to OH^- and that O_2H^- in solution is easily reduced to OH^- at $LaNiO_3$ with no isolated phase.

Discussion

The rate Eq. 1 holds for the Hoare path of the O_2 reduction at $LaNiO_3$, as described in previous papers.[1,2,14] Then the following reaction scheme will be valid:

$$O_2 \rightarrow O_2(\text{ad}), \tag{2}$$

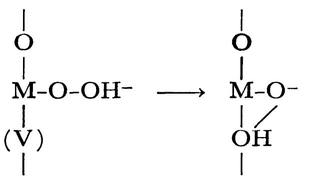
$$O_2(\text{ad}) + e \rightarrow O_2^-(\text{ad}), \tag{3}$$

$$O_2^-(\text{ad}) + H_2O \rightarrow O_2H(\text{ad}) + OH^-, \tag{4}$$

$$O_2H(\text{ad}) + e \rightarrow O_2H^-(\text{ad}). \tag{5}$$

The rate determining step was found to be step (5) when the Tafel relation holds, and (2) for the limiting current case.[1] Presnov *et al.*[15] proposed the feasibility of a reaction scheme similar to that proposed here from a general treatment of oxide catalysts on the basis of a knowledge of coordination chemistry.

Any step subsequent to (5) has to conform to the experimental result of non-detection of O_2H^- in the electrolyte. The rearrangement of adsorbed O_2H^- on the electrode surface in a manner such as that shown in Eq. 6 seems to be feasible for the formation of OH^-:



$$\text{M-O-OH}^- \longrightarrow \text{M-O}^- \tag{6}$$

Here (V) denotes an O^{2-} ion vacancy on the oxide surface. If step (6) does rapidly occur, the desorption of O_2H^- (ad) will not take place, and hence no detection of dissolved O_2H^- is possible at the ring electrode. In this case the electron transfer from the electrode to the σ^* orbital of the adsorbed O_2H^-, which follows step (6), must destroy its σ bond and then OH^- will be produced. Such a mechanism seems to fit well for preferential reduction of O_2 to OH^- at $LaNiO_3$.

In the process of the rearrangement of the adsorbed O_2H^- (Eq. 6), an O_2^- ion vacancy is required at the oxide surface. In the case of $LaNiO_3$, the surface composition may be represented as $LaNiO_{3-\delta}$, where δ is the deficiency of O^{2-} from the stoichiometric composition and was about 0.2 to 0.3 in the O_2 reduction potential region[9] Therefore, step (6) is likely to take place. The results that O_2 was completely reduced to OH^- and that the reduction of O_2H^- proceeded quite easily at this oxide seem to be reasonable in the light of the mechanism proposed.

Co_2O_3, Co_3O_4, and Ni_3O_4 seem to have a fairly large number of O_2^- vacancies; but not so with NiO and CoO when these oxides are polarized in alkaline solutions in potentials less positive than about 0.9 V, in which the O_2 reduction proceeeds,[6,7] because thermodynamically NiO and CoO are very stable in this potential region. It was reported that the O_2 reduction at cobalt mixed oxides (CoO+Co_2O_3), Co_2O_3, and Co_2NiO_4 gave no appreciable amount of O_2H^- and that O_2H^-, when added to an electrolyte, was easily reduced at these oxides.[6,7] On the contrary, the O_2 reduction at NiO gave O_2H^-, and O_2H^- was not reduced to OH^-.[6,7] These results, therefore, support the necessity of O^{2-} vacancies for the O_2 reduction. In the case of the mixed cobalt oxides, O_2H^- might be produced on the CoO phase but it must immediately be reduced further to OH^- on the co-existing Co_2O_3 phase. Because of this, the ring current is believed to have been detected only very faintly.[6,7]

It is predicted from the above discussion that O_2 is completely reduced to OH^- at $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Sr_xCoO_3$ catalysts[16,17] in alkaline solutions, because these oxides have some O^{2-} vacancies in the potential region where the O_2 reduction proceeds.

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