

CHARACTERIZATION OF OXYGEN ELECTRODES WITH CARBON BLACK CONTAINING AS CATALYST METAL OXIDE

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1. Introduction

In previous paper [1] we have reported that an electrode with carbon black modified by anodic oxidation showed good electrode performance compared with untreated one, because of the high decomposition ability of hydrogen peroxide and adequate wettability control. In this paper we will report the relationship between the surface properties such as electric conductivity, hydrogen peroxide decomposition rate of some metal oxides, and the performance of carbon black electrodes containing as catalysts the oxides. An interesting electrode reaction mechanism arising from the polarization measurements of oxygen reduction by use of a rotating ring-disk electrode in an aqueous alkaline solution has also been discussed.

2. Experimental

Commercial acetylene black (AB) was chosen as the sample carbon black. Double layered gas diffusion electrode [2] with fixed gas supplying-layer were prepared by hot-pressing carbon black with poly(tetrafluoroethylene) (PTFE) as a binder. Electrochemical reduction of oxygen was carried out by the potential sweep method at 25°C in a 1 mol/dm³ KOH aqueous solution. The potential sweep rate was 20mV/min. The flow rate of oxygen was kept at 100cm³/min throughout the experiments.

A designed rotating ring-disk electrode (RRDE) is shown in Fig. 1. The RRDE was constructed so that the silver disk plane was depressed by 0.5 mm from the outer face of the electrode. In the cavity formed between the disk and the PTFE insulating ring, a paste containing about 3 g liquid paraffin per g of carbon powder was introduced.

Electrical conductivity was measured by using an ac bridge of 1 kHz. The prepared carbon samples were put into a quartz glass tubing with two stainless steel terminal electrodes. The designed apparatus was used for determining the rate constant of hydrogen peroxide decomposition. The constant volume of a 3 % H₂O₂ solution was added to an Ehrlenmeyer flask containing 50 mg of sample. The amount of oxygen was measured by using a gas burette at 25 °C in an air bath.

3. Results and Discussion

The electrochemical parameters obtained from the RRDE

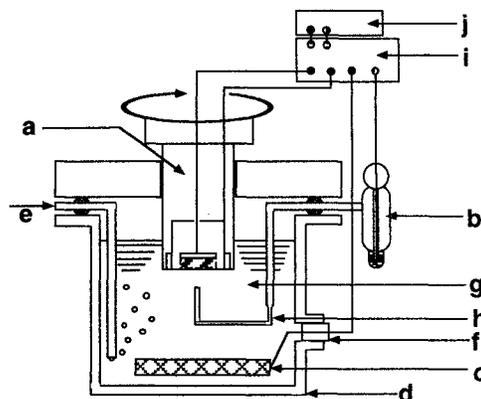
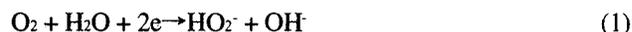


Fig. 1. Apparatus for polarization measurement by using rotating ring-disk electrode. (a) Rotating ring-disk electrode, (b) reference electrode (Hg/HgO), (c) counter electrode (Ni), (d) pyrex glass cell, (e) O₂ gas inlet, (f) silicone rubber stopper, (g) 1 mol/dm³ KOH aqueous solution, (h) luggin capillary, (i) potentiostat, (j) recorder

experiment and the surface properties of the samples are summarized in Table 1. The rate constants of two kinds of metal oxides, LaMnO₃ and LaCoO₃, were about 60 ~ 110 times larger than that of AB. Such an increase of H₂O₂ decomposition ability on the catalyst surface would result in a good performance of the oxygen electrode, i.e. it may be preferable for the decomposition of HO₂⁻ formed by a charge transfer reaction,



The low electrical conductivity of the metal oxides would be a negative factor for oxygen electrode performance. Accordingly, we need to find out the optimum amount of addition of the catalysts.

Figure 2 shows the polarization curves of oxygen electrodes with AB containing as catalyst metal oxide. As shown in Fig. 2, the activation polarization of the electrode with metal oxide was much better than that of the carbon electrode without the catalyst. This can be explained by the fact that the electrode with the metal oxide has a high H₂O₂ decomposition ability.

In alkaline electrolyte, oxygen reduction may proceed via a four-electron process to hydroxide ions or via a two-electron process to peroxide ions or a combination of the above [3].

Table 1. Electrochemical parameters obtained from RRDE method and surface properties of samples

Samples	n	k_1/k_2	k_3+k_4	k_w ($10^{-3}/s/g$)	σ (S/cm)
AB	2.0	0.51	≈ 0	0.057	6.8
LaMnO ₃	2.4	5.06	≈ 0	6.24	3.5×10^{-4}
LaCoO ₃	2.7	0.54	> 0	3.39	6.1×10^{-4}

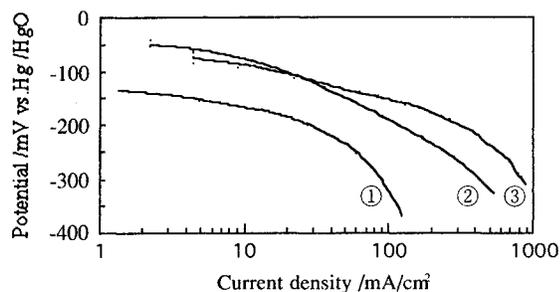
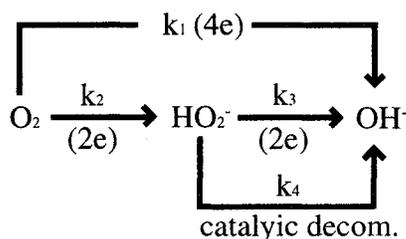


Fig. 2. Polarization curves of oxygen electrodes with AB containing as catalysts metal oxides

① AB, ② LaMnO₃, ③ LaCoO₃



estimate the ratio of reaction rate constants, k_1/k_2 and the sum of those, k_3+k_4 from eqns (4) and (5).

$$N(i_d/i_r) = 1 + 2k_1/k_2 + A + AM\omega^{-1/2} \quad (4)$$

$$A = \alpha \{2k_1k_2(k_3+k_4) + (2k_3+k_4)\} \quad (5)$$

Where N is collection efficiency. Both M and α are constants. The electrochemical parameters obtained are summarized in Table 1. From the results of this RRDE experiment it can be concluded that: i) The electrochemical oxygen reaction on AB electrode is a two electron reaction forming HO_2^- , ii) With LaMnO₃, the oxygen reduction would be a combination of two and four electron reactions because $n=2.4$ and $k_1/k_2 > 1$, iii) With LaCoO₃, the reaction may be a two electron reaction because $k_1/k_2 < 1$ and $k_3+k_4 > 0$. But intermediate HO_2^- would change to OH^- and O_2 because the k_w is larger than that of AB.

To investigate the reaction mechanism of oxygen reduction, the polarization experiment by using RRDE was performed. A typical example of i_d -E curves obtained in a 1 mol/dm³ KOH solution as a function of rotation speed is shown in Fig. 3. Assuming that the electrochemical reduction of oxygen is first order against the concentration of dissolved oxygen in an alkaline electrolyte, a relation between i_d and rotation of a disk electrode is written by the equation

$$1/i_d = 1/i_k + 1/B\omega^{-1/2} \quad (2)$$

$$B = 0.62nFC_0D^{2/3}\nu^{-1/6}S(2\pi/60)^{1/2} \quad (3)$$

where i_k is reaction current and n is the number of electrons for the electrochemical reduction of 1 mol of oxygen. C_0 , D , ν , F and S are oxygen concentration, diffusion constant, kinetic viscosity, Faraday constant and disk area, respectively. We can obtain the n value of each sample electrode from the linear relation of eqn 2. Also, we can

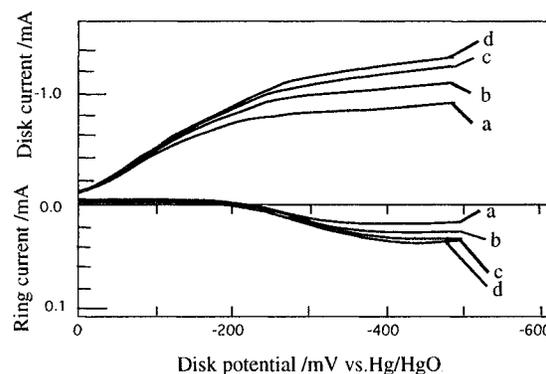


Fig. 3. Rotating ring-disk currents for O₂. Reduction on AB past with or without LaMnO₃
Rotation per minute: (a) 400, (b) 800, (c) 1200, (d) 1600

References

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