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Effect of Electrochemical Pretreatment on Catalytic Activity of Bismuth Ruthenate Electrodes for Oxygen Evolution in Alkaline Solution

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The catalytic activity of a film-type bismuth ruthenate electrode for oxygen evolution was greatly enhanced by the electrochemical pretreatment, including potential holding and cycling. On the other hand, any appreciable enhancement in catalytic activity was not observed for a pellet-type bismuth ruthenate electrode. Such an pretreatment effect was explained on the basis of the participation of higher valence Ru species in the oxygen evolution reaction, rather than the increase of surface area.

Metallic oxides with the pyrochlore structure such as bismuth and lead ruthenates ($Bi_2Ru_2O_7$, $Pb_2Ru_2O_{7-y}$) have been of increasing interest as electrode materials in recent years. Carcia et al.[1] have first reported that bismuth ruthenate thin film electrodes, prepared by rf sputtering directly onto heated Ti substrates, showed high activity for chlorine evolution. On the other hand, Horowitz et al.[2] have lately reported that in alkaline electrolyte bismuth and lead ruthenates, prepared mainly by the alkaline solution synthesis technique, displayed significantly lower polarizations than any other catalyst for oxygen evolution and were among the best for oxygen reduction. The oxygen reduction on bismuth and lead ruthenates, prepared by conventional solid state synthesis technique, has also been reported by Egdell et al.[3]

In the course of the studies on DSA-type metal oxide electrodes for oxygen evolution, we noticed that bismuth ruthenate film electrodes showed high catalytic activity for the reaction when they were pretreated electrochemically. The pretreatment included the potential holding and cycling. To date, the electrocatalytic activation of noble metal electrodes for oxygen and chlorine evolution reactions by potential cycling has been studied rather extensively.[4—10] However, many different interpretations have been proposed for the cause of the activity enhancement. The arguments seem to be principally divided into two groups: (1) Apparent activity enhancement by the increase in surface area and (2) intrinsic activity enhancement by the surface modification. This paper describes the work on the effect of electrochemical pretreatment on catalytic activity of bismuth ruthenate electrodes for oxygen evolution in alkaline solution, supporting the second view rather than the first view.

Experimental

Film- and pellet-types of bismuth ruthenate electrodes were used in this work. The film-type electrode ($Pt/Bi_2Ru_2O_7$) was prepared by a thermal decomposition method in the following way. First, a Pt substrate ($2.5_4\,cm^2$) was mechanically polished with emery papers (≈#2000) and then degreased with a boiling 1 mol dm^{-3} KOH aqueous solution. Next, 0.05 cm^3 of (0.05 mol dm^{-3} $BiCl_3$ and 0.05 mol dm^{-3} $RuCl_3$)-containing 20 wt% HCl aqueous solution was applied to one side of the cleaned Pt substrate, dried at temperatures below 100 °C and then heated at 700 °C in air for 10 min. Such operations were repeated for 5 times. Finally, the resulting sample was heated at 700 °C for 1 h to decompose completely. On the other hand, the pellet-type electrode ($Bi_2Ru_2O_7$) was prepared by a coprecipitation method in the following way. First, the above mixed solutions of $BiCl_3$ and $RuCl_3$ were hydrolyzed by adding concentrated ammonia water. The resulting coprecipitate was washed thoroughly with distilled water and then dried at temperatures below 100 °C. Next, the dried sample was heated at 700 °C in air for 10 min, followed by grinding to powder with an agate mortar and a pestle. After such operations were repeated for 5 times, the powder was heated at 700 °C for 12 h. Finally, the heat-treated powder was mixed with 15 wt% of a binder (mp ca. 283 °C) and then pressed at 6000 kg cm^{-2} to form a pellet (1.3_3 cmϕ, ca. 0.05 mm thick). The pellet was heated at 240 °C and water-proofed by immersing in 10 wt% polystyrene-containing benzene solution. The X-ray diffraction patterns of the surface oxides of the electrodes thus obtained correspond to the formula $Bi_2Ru_2O_{7.3}$ as indicated in the ASTM card, however, the bismuth ruthenate electrodes will be represented by $Pt/Bi_2Ru_2O_7$ or $Bi_2Ru_2O_7$ in this paper because the oxygen content is still uncertain.

All electrochemical measurements, including cyclic voltammetry and polarization measurements, were carried out at 30 °C in 1 mol dm^{-3} KOH aqueous solution unless otherwise stated. The counter electrode used was a Pt plate with large surface area. A mercury (II) oxide electrode (Hg/HgO, 1 mol dm^{-3} KOH) was mainly used as the reference electrode.

The other experimental procedures and conditions will be described in the next section.

Results and Discussion

The film-type $Pt/Bi_2Ru_2O_7$ electrode was previously anodized at a constant potential (typically 0.7 V vs. Hg/HgO) for several tens minutes (typically 40 min). For each 10 min, the potential was cycled twice in the region between 0 and 0.7 V vs. Hg/HgO with a sweep rate of 0.1 V s^{-1} in order to check the catalytic activity. However, the potential cycling should also be regarded as a part of the pretreatment because the pretreatment effect described later was not observed in the absence of the succeeding potential cycling (see Fig. 6) and because the same effect was observed when the potential cycling was continued for much longer time (say 50 min) without the preceding constant-potential anodization.

Typical cyclic voltammograms of the Pt/$Bi_2Ru_2O_7$ electrodes with and without pretreatment are shown in Fig. 1. It is evident that the current, or the catalytic activity, for oxygen evolution is appreciably enhanced by the pretreatment. Such a current enhancement phenomenon is not explicable by the change of surface area alone, because the surface area of the pretreated electrode was found to be only about 1.3 times that of the non-pretreated electrode as the result of the surface area determination both by Zn^{2+} ion adsorption method[11] and by cyclic voltammetry[12] and because the current enhancement was observed in alkaline solutions with relatively high pH values but scarcely in acidic solutions; for example, the electrode pretreated in 1 mol dm^{-3} KOH did not reveal any enhanced activity for oxygen evolution in 0.5 mol dm^{-3} H_2SO_4.

It can also be seen from Fig. 1 that the redox peaks at around 0.4 V vs. Hg/HgO become more conspicuous after pretreatment. The redox peaks may be attributable to either Ru^{4+}/Ru^{5+} or Ru^{4+}/Ru^{6+} as reported for the $Bi_2Ru_2O_7$[3] and Ti/(RuO_2+TiO_2)[13] electrodes, respectively, in alkaline solutions. The current enhancement factor, which was defined as the current density at a given potential (0.7 V vs. Hg/HgO) after pretreatment divided by the current density at the same potential before pretreatment, increased as the preanodization potential increased beyond ca. 0.4 V vs. Hg/HgO where the redox peaks appeared (see Fig. 1). Furthermore, a positive correlation was observed between the current enhancement factor and the charge passed in the redox peaks. These facts suggest the important role of the mixed valence Ru species in the pretreatment effect, in agreement with the view reported for the other kinds of electrodes.[4,7,8,10]

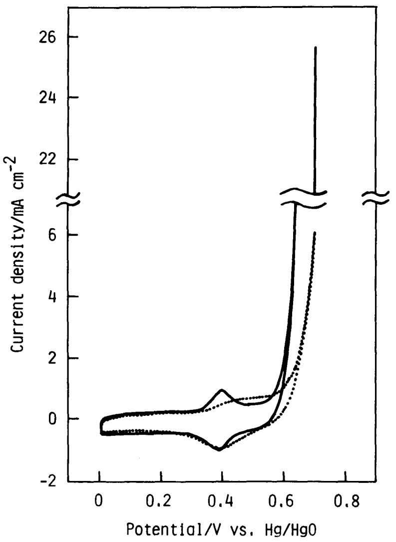

Fig. 1. Cyclic voltammograms of the film-type Pt/$Bi_2Ru_2O_7$ electrodes with (solid line) and without (dotted line) pretreatment, measured in 1 mol dm^{-3} KOH (sweep rate=100 mV s^{-1}).

The film-type electrodes having different oxide compositions were prepared by changing the mole ratio of $BiCl_3$ to $RuCl_3$ while the total amount of them was kept constant at 1×10^{-5} mol cm^{-2}, and their catalytic activities for oxygen evolution were measured. Figure 2 shows the plots of current density at 0.7 V vs. Hg/HgO against Bi content in the oxide layer for the Pt/$Bi_xRu_{1-x}O_y$ ($0\leqslant x\leqslant 1$) electrodes with

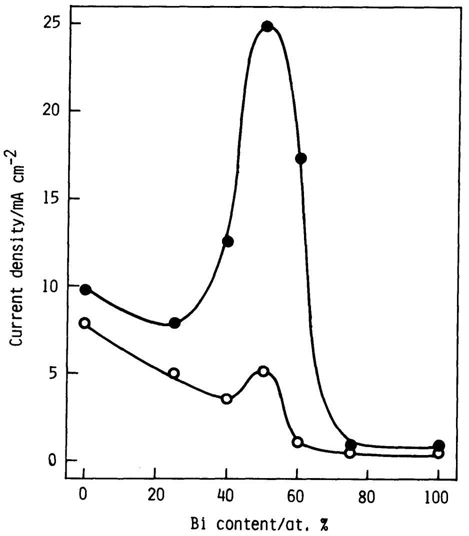

Fig. 2. Plot of current density at 0.7V vs. Hg/HgO against Bi content for the film-type Pt/$Bi_xRu_{1-x}O_y$ ($0\leqslant x\leqslant 1$) electrodes with (closed circle) and without (open circle) pretreatment.

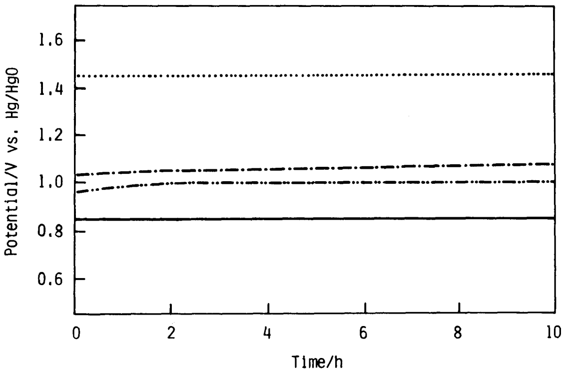

Fig. 3. Potential-time curves of the film-type Pt/$Bi_2Ru_2O_7$ and related electrodes under constant-current (0.1 A cm^{-2}) polarization in 1 mol dm^{-3} KOH. ......: Pt, —·—: Pt/$Bi_2Ru_2O_7$, —··—: Pt/RuO_2, ——: pretreated Pt/$Bi_2Ru_2O_7$.

and without pretreatment. The current for oxygen evolution has a maximum value at the oxide composition corresponding to $Bi_2Ru_2O_7$. It is to be noted that the catalytic activity for oxygen evolution of the $Pt/Bi_2Ru_2O_7$ electrode is rather low before pretreatment but is quite high after pretreatment, compared with that of the Pt/RuO_2 electrode. The superiority of the pretreated $Pt/Bi_2Ru_2O_7$ electrode over the Pt/RuO_2 electrode as well as the non-pretreated $Pt/Bi_2Ru_2O_7$ electrode in catalytic activity for oxygen evolution was confirmed by constant-current polarization measurements, as shown in Fig. 3 (see also Fig. 4). These findings suggest the special participation of Bi species in the pretreatment effect.

In contrast to the film-type $Pt/Bi_2Ru_2O_7$ electrode mentioned above, the pellet-type $Bi_2Ru_2O_7$ electrode showed no detectable pretreatment effect. Furthermore, the apparent redox peaks were observed on the cyclic voltammograms for the $Bi_2Ru_2O_7$ electrode even in the absence of pretreatment. Figure 4 shows galvanostatic polarization curves of the pellet-type electrodes together with the film-type electrodes. The pellet-type $Bi_2Ru_2O_7$ electrode exhibits the relatively high catalytic activity for oxygen evolution though it shows a steep rise in potential at high current densities, probably because of its low electrical conductivity. These observations are explained on the basis of the assumption that some Ru species exist in higher valence state on the surface of the as-prepared $Bi_2Ru_2O_7$ electrode, as well as the pretreated $Pt/Bi_2Ru_2O_7$ electrode.

The X-ray photoelectron spectroscopic (XPS) measurements were performed to get support for the above assumption. Figure 5 shows some XPS data obtained with the $Pt/Bi_2Ru_2O_7$ and $Bi_2Ru_2O_7$ electrodes. Evidently, the additional Bi peaks observed for the non-pretreated $Pt/Bi_2Ru_2O_7$ electrode in higher binding energies disappear in the case of the pretreated $Pt/Bi_2Ru_2O_7$ electrode, suggesting a valency change of Bi species in part from higher to lower oxidation states. Moreover, the Bi spectra of the pretreated $Pt/Bi_2Ru_2O_7$ electrode are similar to those observed for the $Bi_2Ru_2O_7$ electrode. On the other hand, the Ru spectra except for Ru $3d_{5/2}$ were unfortunately ambiguous for every electrode, due to the contamination by C 1s electron line at 285.0 eV. Though the further detail measurements are necessary, it appears more likely from the information obtained that the pretreatment effect is attributed to the formation of higher valence Ru species and the coexistence of Bi species may contribute to maintain the Ru species in higher valence state.

In order to prove the above view, the pretreatment effect was further examined with the other film-type electrodes ($Pt/Bi_{2-x}Co_xRu_2O_{7-y}$) prepared by partial substitution of Co^{2+} for Bi^{3+}.[14] As a result, the catalytic activity for oxygen evolution of these electrodes was found to be essentially high even before pretreatment and to increase with increasing Co content. The variation of current enhancement factor with preanodization time for the $Pt/Bi_{2-x}Co_xRu_{7-y}$ ($0 \leqslant x \leqslant 0.5$) electrodes is shown in Fig. 6. As expected, the current enhancement factor decreases with an increase in Co content. This can be explained by taking into account the valence change of Ru species by replacing Bi^{3+} with Co^{2+}, in addition to little contribution of Co oxide itself to the increased catalytic activity for oxygen evolution.

The mechanistic analysis was briefly done for the oxygen evolution reaction on the pretreated $Pt/Bi_2Ru_2O_7$ electrode and, as the result, the kinetics were found to be characterized by a Tafel slope of $0.042\ V\ dec^{-1}$ and a reaction order with respect to OH^- ion of 1.12. It can therefore be presumed that the reaction mechanism as well as the rate-determining step is identical to that proposed for the

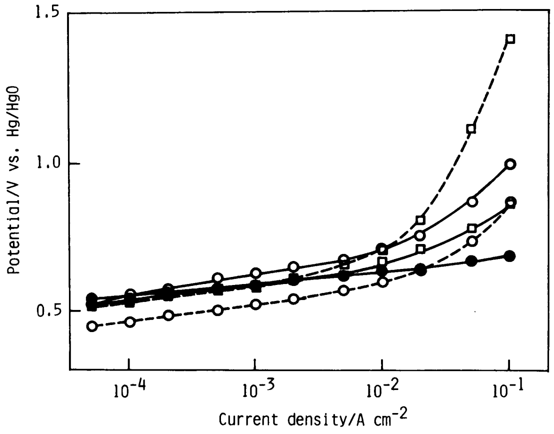

Fig. 4. Galvanostatic polarization curves of the film-type (solid line) and pellet-type(broken line) electrodes in 1 mol dm^{-3} KOH.
○: $Pt/Bi_2Ru_2O_7$, $Bi_2Ru_2O_7$, □: Pt/RuO_2, RuO_2, ●: pretreated $Pt/Bi_2Ru_2O_7$.

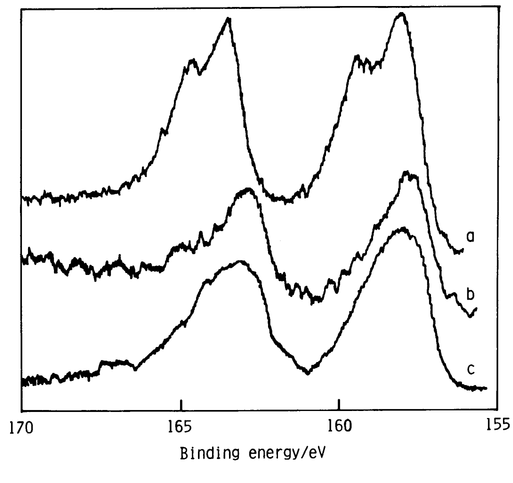

Fig. 5. XPS Bi $4f_{5/2,7/2}$ spectra of (a) $Pt/Bi_2Ru_2O_7$, (b) pretreated $Pt/Bi_2Ru_2O_7$ and (c) $Bi_2Ru_2O_7$ electrodes.

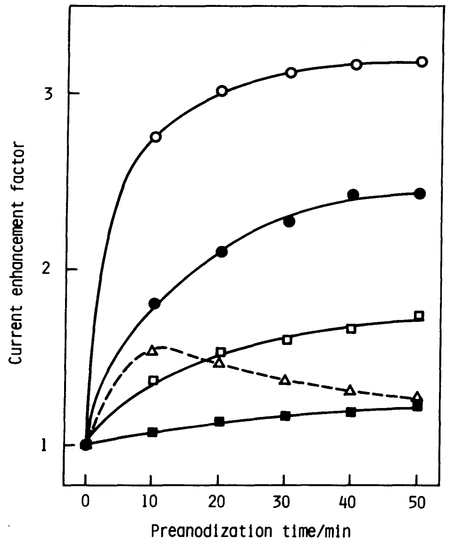

Fig. 6. Variation of current enhancement factor at 0.7V vs. Hg/HgO with preanodization time for the film-type $Pt/Bi_{2-x}Co_xRu_2O_{7-y}$ $(0 \leqslant x \leqslant 0.5)$ electrodes. ○: $x=0$, ●: $x=0.1$, □: $x=0.2$, ■: $x=0.5$.
The broken line with triangles repersents a current enhancement factor vs. time curve for the $Pt/Bi_2Ru_2O_7$ electrode under constant-potential (0.7V vs.Hg/HgO) polarization.
The current enhancement factors are normalized to the values at a preanodization time of 0 min.

Ti/RuO_2 electrode,[15] in which the valence change of Ru species is virtually involved. According to such a mechanism, it is reasonable to expect that higher valence Ru species should cause modification of electron transfer rates and probably of adsorption of intermediates.

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