Oxygen Evolution on $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ Series Oxides

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$\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ series oxides with perovskite type structure were synthesized and were examined as the electrode for the oxygen evolution reaction in alkaline solution. The oxides except for LaFeO_3 were suitable for the electrode material in nature of high conductivity. The catalytic activity for the oxygen evolution reaction increases with increases in x and y values in the composition region of the perovskite single phase. The catalytic activity of the perovskite oxide depends on the σ^* band width and the positive charge density of the transition metal cation on the electrode surface. In addition, it is demonstrated that the perovskite structure is desirable for the high catalytic activity for the oxygen evolution reaction.

1 Introduction

The anodic evolution of oxygen is of special importance in water electrolysis, because an activation overpotential at the electrode is the chief cause of efficiency loss in this process. Some of the perovskite type oxides with high electronic conductivity show good catalytic activity for the oxygen evolution reaction¹⁻⁷⁾ and the oxygen reduction⁸⁻¹⁰⁾. In particular, the perovskite type oxides containing Co, Fe and Ni ions in the lattice are excellent in the catalytic activity for the oxygen evolution reaction in alkaline solution^{2-4,6)}. For example, the electrodes of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ series oxides with large x and y values bring about low overvoltages for the oxygen evolution reaction. From the variations of the catalytic activity with x and y values in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ series oxides, it is concluded that as for the oxygen evolution reaction, 1) the σ^* band formation and 2) the higher oxidation state of the transition metal ion in an oxide are desirable for the high catalytic activity¹⁻⁶⁾. The conditions 1) and 2) give favorable effects on the electron transfer steps and the chemical reaction steps in the oxygen evolution process, respectively.

In this paper, the catalytic properties of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ series oxides for the oxygen evolution reaction in alkaline solution are studied. According to the above theory, it is predicted

that the catalytic activity for the oxygen evolution reaction will increase with increases in x and y values in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ oxides. As a result, the catalytic activity obeys this theory in the composition region of the perovskite single phase, but not in the composition region of the mixed oxides phase with or without the perovskite type oxides. Therefore, the favorable effect of perovskite type structure on the catalytic activity for the oxygen evolution reaction is also demonstrated in this paper.

2 Experimental

$\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ series oxides were synthesized by using La_2O_3 , SrCO_3 , Fe_2O_3 and NiO as the starting materials. These materials were mixed in stoichiometric quantities with agate mortar and then heated at 1000°C for 2h in air. The mixtures were reground and heated at $1250^\circ\text{C}\sim 1300^\circ\text{C}$ for 6h in air. The prepared oxides were checked by X-ray analysis with a scanning rate $2\theta/\text{min}^{-1}=2^\circ/\text{min}^{-1}$. The oxides were pressed into tablet form with 100 kg cm^{-2} , followed by sintering at 1350°C for 1h. The porosities of all samples were about 20%. The compositions of the prepared oxides are represented as ABO_3 in this paper for convenience sake, whether the perovskite is produced or not. The specific resistivities at room temperature were measured by four probe method. The types of conductivity of the sample in the vicinity of room temperature were determined from the temperature dependence of the resistivity. The types of semiconductivity, n or p , were judged from the signs of the measured thermo-

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electric powers.

The electrodes were prepared by the same manner as described in previous papers^{2-4,6)}. The current densities shown in this paper will be indicated by the apparent one based on the geometrical area. The solution was pre-electrolyzed 1 M KOH. A Hg/HgO electrode was used as a reference electrode and electrode potentials cited in this paper are referred to this electrode. The main electrochemical test was made by the potential sweep method with a sweep rate of 2 mVs⁻¹ at 25°C. The Tafel slopes were obtained from the polarization curves measured by the same manner as described in previous papers¹⁻⁶⁾.

3 Results

The oxides prepared in the present study are denoted by the symbol of circle in Fig. 1, which shows the phase diagram giving the composition region of the perovskite formation

Fig. 1 Composition region of the perovskite formation in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ series oxides. The circles denote the compositions of the oxides prepared in this study

- (A): The composition region of the perovskite single phase
- (B): The composition region of the mixed oxides phase with perovskite
- (C): The composition region of the mixed oxides phase without perovskite

in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$. The part (A) indicates the composition region of the oxides consisting of the perovskite single phase. The other parts, (B) and (C), are the composition regions of the mixed oxides phase. The perovskite oxides are contained in the composition region (B), but not in the composition region (C). In the mixed oxides phase, NiO , NiLa_2O_4 , and Sr_2FeO_4 were formed. It is found from this figure that the formation of the perovskite oxide becomes more difficult in the composition region with large y values, *i. e.*, with a large amount of Ni.

The phase diagram for resistivity is shown in Fig. 2. The oxides containing a large amount

Fig. 2 Distribution of the resistivity at room temperature. The unit for the each value in the figure is Ωcm

of Ni could not be so tightly sintered. Each of the oxides except for LaFeO_3 has a relatively low resistivity. The resistivity of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ decreases with increases in x and y values in the composition region of the perovskite single phase.

According to Goodenough's theory¹⁷⁾, the conductivity of the perovskite oxide having the composition of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ is determined by the degree of interaction between the transition metal ion and the oxygen ion in its lattice. The degree of interaction increases with increases in x and y values, leading to the increase of conductivity with increases of these values. The tendency of the measured

resistivity in the perovskite single phase is well explained by this theory.

The higher resistivities of the mixed oxides compared to the perovskite type oxides will be based on the presence of the other oxides with low conductivity: NiO , Sr_2FeO_4 , and La_2NiO_4 are semiconductor or insulator. If only a perovskite is formed in the composition regions of the mixed oxides phase, the resistivity will decrease with increases in x and y values. In any cases, the resistivities of the oxides in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ are relatively low, and are suitable for use as the electrode material.

Figure 3 shows the types of conductivity of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ series oxides. All oxides

Fig. 3 Type of the conductivity. The shaded part indicate "semi-metal" with small thermoelectric power

synthesized in this study showed the semiconducting type in this measurement. However, the thermoelectric powers of the oxides in shaded parts are small, in line with the low resistivity of the oxides in this part as shown in Fig. 2. Therefore, these oxides are denoted as "semi-metal" in this figure. In the composition region of the perovskite single phase, the semiconducting type converts at about $x=0.5$ from p -type (in the region of $x<0.5$) to n -type (in the region of $x>0.5$) except for $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$, but is independent of the change of x and y values in the other

regions. The result obtained in the former region is similar to that obtained for $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ series oxides⁹⁾. The ratio of La ion to Sr ion in the lattice may be responsible for the semiconducting type. However, the kind of this type gives no effect on the catalytic property for the oxygen evolution reaction as shown in Fig. 5 and 6. In any case, the semiconducting property, especially rectification, was not observed in the electrochemical tests, because of the degeneration of surface due to a large amount of surface states formed on a sintered disc sample.

Figure 4 shows the voltammogram of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ electrode in 1 M KOH at 25°C.

Fig. 4 Potential sweep voltammogram of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ electrode in 1 M KOH at 25°C

The other oxide electrodes except for LaFeO_3 also showed the similar voltammogram to Fig. 4. The voltammogram was taken in a restricted potential region between 0 V and the potential at which the oxygen evolution current density exceeds about 65 mA cm^{-2} .

Figure 5 and 6 show the phase diagrams for overvoltages (η) of the oxygen evolution reaction at 40 mA cm^{-2} and 60 mA cm^{-2} , respectively, which were determined from the voltammograms measured under the same condition as Fig. 4. The contour lines of overvoltages in this figure shows that the catalytic activity increases with increases in x and y values in the composition region of the perovskite single phase. This

Fig. 5 Distribution of overvoltage (η) at 40 mA cm^{-2} . The unit is mV

(a) : $\eta \leq 500 \text{ mV}$, (b) : $500 \text{ mV} < \eta \leq 550 \text{ mV}$, (c) : $550 \text{ mV} < \eta \leq 700 \text{ mV}$, (d) : $700 \text{ mV} < \eta \leq 800 \text{ mV}$, (e) : $800 \text{ mV} < \eta \leq 900 \text{ mV}$, (f) : $\eta > 900 \text{ mV}$

Fig. 6 Distribution of overvoltage (η) at 60 mA cm^{-2} . The unit is mV

(a) : $\eta \leq 600 \text{ mV}$, (b) : $600 \text{ mV} < \eta \leq 800 \text{ mV}$, (c) : $800 \text{ mV} < \eta \leq 900 \text{ mV}$, (d) : $900 \text{ mV} < \eta \leq 1000 \text{ mV}$, (e) : $1000 \text{ mV} < \eta \leq 1400 \text{ mV}$, (f) : $\eta > 1400 \text{ mV}$

result is in line with that of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ series oxides⁶). However, the catalytic

activity in the other composition region decreases with increase in y value. From the comparison with Fig. 1, it is judged that the decrease of the catalytic activity in this region is attributed to the imperfect formation or unformation of the perovskite. In other words, the perovskite oxide is responsible for the high catalytic activity for the oxygen evolution reaction in structure.

4 Discussion

The mechanism for the oxygen evolution reaction on the perovskite type oxides in alkaline solution is proposed as follows¹⁻⁶).

where M_s stands for the transition metal ion on a surface. The rate controlling will be the 2nd step in the above process for SrFeO_3 and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ electrodes^{2,3}). The rate controlling will be the 3rd step for $\text{SrFe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ and $\text{SrFe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ electrodes and will be the 1st step for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{SrFe}_{0.9}\text{Mn}_{0.1}\text{O}_3$ electrodes as described in the previous papers^{1,4}). In addition, it was presumed in our recent work that the rate controlling is the 2nd or the 3rd step for $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ electrodes⁶). The

Fig. 7 Distribution of Tafel slope for the oxygen evolution reaction. The unit is mV per decade

values of the Tafel slopes of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ series oxides for the oxygen evolution reaction are in the range of about 40~60 mV per decade except for some oxides as shown in Fig. 7. Under the assumption of Langmuirian adsorption condition, this result suggests that the rate controlling is the 2nd or the 3rd step for $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ electrodes in analogy with $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ electrodes^{18,19}.

The rate of the 2nd step is determined by the positive charge density of the transition metal cation on the electrode surface: The rate increases with increase of the positive charge density of the transition metal cation which increases with increase in x value in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$. On the other hand, the rate of the 3rd step is determined by the rate of electron transfer which will be controlled by the σ^* band width¹⁻⁴: The rate increases with increase of the σ^* band width which will increase with increases in x and y values. In any case, the rates of the 2nd and the 3rd steps increase with increases in x and y values in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$, so the catalytic activity for the oxygen evolution reaction increases with increases in x and y values. The above expected tendency of the catalytic activity *i.e.*, the catalytic activity increases from LaFeO_3 to SrNiO_3 in composition, is experimentally obtained in the composition region of the perovskite single phase, but not in those of the mixed oxides phases as shown in Fig. 5 and 6. Favorable effect of the perovskite structure on the catalytic activity will be based on the symmetry of the d -orbitals of the transition metal ion in this structure. The d -orbitals, especially e_g orbitals, of the transition metal ions on the perovskite oxide surface will interact most strongly with the species adsorbed on a surface, if the symmetry of the d -orbitals in the bulk is maintained on a surface. This is because the good symmetry

of the d -orbitals lead to large overlap integral between the orbitals of the transition metal ion and the oxygen ion. The rates of the 2nd and the 3rd reaction steps will increase with increase of the interaction. This will be a main reason for favorable effect of the perovskite structure on the catalytic activity for the oxygen evolution reaction.

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