MEASUREMENTS OF ELECTRICAL PROPERTIES OF AIR ELECTRODE MATERIALS OF SOFC

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ABSTRACT

The electrical conductivities $\sigma$ and the Hall coefficients $R_H$ of lanthanum perovskite-type oxides $La_{1-x}Sr_xMnO_3$ have been measured between 200 and 800 °C in air. The oxides showed the p-type semiconductor properties and also the magnetoresistance effect. $R_H$ has a positive sign and varies according to the magnitude of the applied magnetic field. The concentrations of carriers in the oxides were also estimated.

INTRODUCTION

The mechanism of electrical conduction in lanthanum perovskite-type oxides such as $La_{1-x}Sr_xMnO_3$ has been the major subject of investigations with regard to the development of air electrode materials for solid oxide fuel cell (SOFC). In spite of their excellent thermal coordination with YSZ electrolyte in a wide temperature range, there still remains many problems to be solved on the improvements of electrical properties. The electrical conductivity of the oxides can be improved by substituting Sr dopant in La site. $La_{1-x}Sr_xMnO_3$ gives maximum electrical conductivity in the case of $x = 0.3$ and also shows ferromagnetism. These phenomena are more interesting than other perovskite-type oxides such as $La_{1-x}Sr_xCoO_3$, as they have higher conductivities and show paramagnetism [1].

In this paper, the types of major charge carriers and their concentrations in the oxides $La_{1-x}Sr_xMnO_3$ ($x = 0.1, 0.3$), were revealed by the Hall coefficient measurement. Investigations on the mechanism of comparatively high electrical conductivity at higher temperatures were furthermore discussed.

EXPERIMENTAL

Preparation of Samples

The perovskite-type oxides $La_{1-x}Sr_xMnO_3$ were synthesized using the oxides $La_2O_3 , SrO$ and $Mn_2O_3$ (Kojundo Kagaku) as starting powders. The oxide powders were weighed and mixed for 6 hours, and then sintered at 1350 °C in the electric furnace for 24 hours. X-ray
Diffraction patterns were taken for the sintered powders with a powder diffractometer at room temperature using Cu-$k_\alpha$ radiation. Crystalline structures were confirmed by comparing the patterns with JCPDS cards. The powders, -400 mesh, were pasted on the surface of YSZ disk (20 mm $\phi$) by PVA slurry, and then sintered at 1500 °C for 10 hours in the electric furnace to obtain dense sintered membranes.

Four electrodes were attached on the surface by Pt paste, and Pt lead wires were connected. The obtained specimens were rigidly held on the alumina plate holder. Fig 1 shows the sketch of a sample and the configuration of measurement.

Experimental Circuit

The sample was set in the center of the electric furnace (50 mmt, 100 mmL, 80 mmH) and heated up to 800 °C by 4 SiC heater rods. Both sides of the electric furnace were cooled by water cooler made of copper. The furnace was held in the center of the magnet gap (60 mmL) as shown in Fig. 2. In this experiment, the two considerable spurious effects were removed carefully. The direction of heating direct current of heater rods was controlled in order to cancel the magnetic field associated with it at the sample. The uniformity of the magnetic field on the surface was checked out. The sample and the lead wires were tightly held so as to avoid the movement caused by the magnetic force by the applied magnetic field. The voltage electrodes were held horizontally in order not to cause a temperature difference between them and to eliminate Seebeck voltage [2] [3]. Considerations to the length of Pt lead wires to decrease the heat loss from them so as not to make serious temperature changes at the electrodes was also given.

The magnetic field was varied from 500 G to 3000 G, and the temperature was changed between 200 °C and 800 °C. The Hall voltage was measured by the conventional van der Pauw method [4]. The Hall coefficient was determined by averaging values obtained by reversing the direction of direct current.

Fig. 3 shows the outline of the measurement circuit of the Hall coefficient.

Theoretical

The electric field $E$ and the magnetic field $B$ are perpendicular to each other, and their relationships are represented in the cartesian coordinate system as follows [5],

$$\begin{pmatrix} j_x \\ j_y \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ -\sigma_{xy} & \sigma_{yy} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix}$$

(1)

where $E = (E_x, E_y, 0)$, $J = (j_x, j_y, 0)$: current density, $B = (0, 0, B_z)$: $\sigma_{xx}, \sigma_{xy}, \sigma_{yy}$ are tensors and functions of $B$.

From the eq.(1), the Hall coefficient was defined by $E_y$ in case $j_y = 0$ as,
\[
R_H(B) = \frac{E_y}{B_z j_x} = \frac{E_y}{B_z E_x j_x} = \frac{E_y}{B_z E_x \sigma_x}
\]

where \( \sigma_x \) is the electrical conductivity in the applied magnetic field.

From this equation, the Hall coefficient could be considered to be the function of B, and the following equation regarding the oxide semi-conductors could be obtained approximately,

\[
R_H^0 = R_H (B \to 0) \equiv -\frac{1}{ne}
\]

where \( n \) : concentration of charge carrier, \( e \) : charge

RESULTS

Conductivities and Type of Carrier

In Fig.4(a), experimental results of typical electrical conductivity changes under various oxygen concentrations of \( \text{La}_{1-x} \text{Sr}_x \text{MnO}_3 \) \( (x=0.1) \) have been plotted as a function of \( 1/T \). It could be observed that the oxide has the p-type semiconductor characteristics as the electrical conductivity increases according to the increase of oxygen concentration. The same result also obtained in case of \( x = 0.3 \) oxide. Fig.4(b) shows the boundary effect on the electrical conductivity of the same oxide for 2 kinds of powder particle sizes, -100 mesh and -400 mesh respectively. From this result, the existence of the grain boundary in the oxide membrane does not seriously affect on the electrical properties for a wide temperature range. Fig.4(c) shows the effect of the magnetic field on the electrical conductivity of \( \text{La}_{0.7} \text{Sr}_{0.3} \text{MnO}_3 \) and reveals the increase of the conductivity according to the increase of the magnetic field. The electrical conductivities of the \( \text{La}_{1-x} \text{Sr}_x \text{MnO}_3 \)'s are saturated at higher temperature, over 800 \( ^\circ \)C, and the experimental equation could be represented as following by the least square approximation method,

\[
\sigma = \frac{\sigma_0}{T} \exp \left( -\frac{\phi}{k_B T} \right)
\]

where \( \phi \) : activation energy, \( k_B \) : Boltzmann constant, \( T \) : temperature, \( \sigma_0 \) : constant

Hall coefficient and Carrier

In Fig.5(a) and (b) experimental values of the Hall coefficient \( R_H(B) \) under various magnetic field have been plotted as a function of \( 1/T \) for \( x=0.1 \) and \( 0.3 \) oxide, respectively. \( R_H(B) \) has a positive sign and changes its values according to the magnitude of the applied magnetic field.
The Hall coefficient could be represented as the function of magnitude of the magnetic field because of the magnetic dependency of the electrical conductivity shown in Fig. 4 (c). Fig. 6 represents the relationships of \( R_H (B) \) and B plotted in a semi-log paper over various temperatures. From this, the Hall coefficient \( R_H^0 \) could be calculated and then carrier (hole) concentration could be obtained by equation (3).

In Fig. 7 the calculated hole concentrations \( (n_{0.1}, n_{0.3}) \) for the \( x=0.1 \) and 0.3 oxides have been plotted as a function of T. The hole concentration \( n_{0.1} \) increases with the temperature raise until the saturation occurs nearly 450 °C. This region can be recognized as impurity range. In saturation region, the concentration of holes is approximately \( 8.6 \times 10^{16} \text{ cm}^{-3} \). It increases again from approximately 700 °C. The concentration \( n_{0.3} \) also increases with the same tendency as that of \( n_{0.1} \), but the saturation region can not be observed clearly compared with \( n_{0.1} \) and has a larger value at higher temperatures.

**DISCUSSIONS**

It is known that the electrical conductivity is represented by the following equation,

\[
\sigma = e n \mu_H
\]  
(5)

where \( \mu_H \) is the Hall mobility

The temperature dependence of the electrical conductivity of \( \text{La}_1-x\text{Sr}_x\text{MnO}_3 \) can be expressed by the following equation,

\[
\sigma = \frac{\sigma^0}{T} \exp \left( -\frac{\phi^0}{k_B T} \right)
\]  
(6)

and the activation energies of the oxides can be calculated from \( \sigma - 1/T \) plots. Table 1 gives the experimental result and the activation energies in the impurity range. The energy difference between the activation energy \( \phi^a \) and \( \phi^b \) may be considered to compensate the recombination of electron and hole in the oxide. Following relationship could be also obtained as the \( \phi_a \) has the same value for both oxides \( x=0.1 \) and \( x=0.3 \) in the impurity range,

\[
\frac{\mu_{H_{0.1}}}{\mu_{H_{0.3}}} = \frac{\sigma_{0.1}}{\sigma_{0.3}} \propto \exp \left( -\frac{\phi_{0.1} - \phi_{0.3}}{k_B T} \right)
\]  
(7)

The substitution of Sr seems to be more effective to increase the Hall mobility from equation (7). Fig. 8 shows the temperature changes of \( \sigma, R_H, \mu_H \) and \( n \) in case \( x=0.3 \) oxide vs 1/T in the semi-log graph. From the equation (7) and the Fig. 8, it can be recognized that the increase of the electrical conductivity of \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) is mainly supported by the Hall mobility during impurity range till approximately 400 °C.
This means that the effect of scattering by the ions on the movements of carriers is not so remarkably strong and the carriers could move from one ion after another ion. In the higher temperature range, the increase of the electrical conductivity seems to be supported by the increase of the carrier concentration till approximately 700 °C.

Over 700 °C, the scattering effect of the ions becomes so strong as to prohibit the smooth movement of the carriers and to cancel the effect of the dense carrier concentration. So it can be supposed that the electrical conductivity of \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) could be supported mainly by the oxidation-reduction of Mn ions known as hopping model and represented as following [6],

\[
\text{La}_{1-x}\text{Sr}_x\text{Mn}^{3+}_{1-x}\text{Mn}^{4+}_x\text{O}_3
\]

(8)

The hopping movement of the carriers in the oxide could be considered from the experimental results and discussions.

CONCLUSIONS

1. The Hall coefficients \( R_H \) of the lanthanum perovskite-type oxides \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) could be obtained by the van der Pauw method for a wide temperature range in the air. \( R_H \) has a positive sign and the oxides are to be p-type semiconductor.

2. The electrical conductivity of the oxides has the ferromagnetoresistance and could be supported by the increase of the Hall mobility in the impurity range.

3. In the higher temperature range, the scattering effect of the ions overwhelms the increase of the carrier concentration.

4. The substitution of Sr in the oxides can be more effective to increase the Hall mobility than to increase the carrier concentration.

5. The electrical conductivity of the oxides could be supported by the hopping mechanism.

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Table 1. Summary of experimental data.

| Material       | $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ | $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ |
|----------------|---------------------------------|---------------------------------|
| Conduction type| P-type                           | P-type                           |
| Sign of RH     | +                                | +                                |
| $\phi^0 (eV)$  | 0.197                            | 0.139                            |
| $\phi_n (eV)$  | 0.12                             | 0.12                             |

Fig. 1 Outlook of a sample and configuration of measurement.
Fig. 4(a) Oxygen concentration dependence of electrical conductivity of La$_{1-x}$Sr$_x$MnO$_3$

Fig. 4(b) Effect of powder particle size on electrical conductivity of La$_{1-x}$Sr$_x$MnO$_3$

Fig. 4(c) Effect of the magnetic field on electrical conductivity of La$_{1-x}$Sr$_x$MnO$_3$
Figs. 5 Hall coefficient vs. 1/T

Figs. 6 Hall coefficient vs. magnetic field

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Fig. 7 Carrier concentration vs. Temperature

Fig. 8 Temperature changes of $\sigma$, $R_H$, $\mu_H$ and $n$ in $La_{1-x}Sr_x MnO_3$