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Development of new anion-conducting layered perovskite-type oxide electrolytes

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Layered perovskite oxide $LaSr_3Fe_3O_{10}$ (LSFO) was characterized by electrochemical measurements and XRD. The H_2 sensing property of the oxide with 15wt% Pd/LSFO anode catalyst in H_2 at room temperature was examined. As for H_2 sensing, the potential about 0.9 V was gained in the presence of H_2 without cathode catalyst. Furthermore, the membrane potential for concentration cell of NaOH with LSFO showed negative value, and the potential with anion exchange membrane (AEM) also showed negative value. These results suggest that LSFO shows OH^- conductivity and the possibility of a new type fuel cell by using LSFO as electrolyte.

Introduction

Thermoelectric materials are becoming increasingly important in the field of energy harvesting and conversion. Thermoelectric devices are generally based on heavily doped semiconductors and can be used for cooling applications of for electricity generation directly from a heat source. When supplied by a temperature differential, thermoelectric semiconductors respond by virtue of the Seebeck effect to produce a voltage that could be used to drive an external load. A broad search has been under way to identify new materials with enhanced thermoelectric properties.

Sodium cobalt oxide, $NaCo_2O_4$ (NCO) has received considerable attention due to its unusual thermal electric properties [1]. NCO pellets with anodes consisting of 15wt% Pd/NCO showed reasonable potential in oxygen excess atmosphere, we can convert the catalytic combustion heat to electrical energy by usual thermoelectric conversion. However, the potential in hydrogen excess atmosphere showed 0.8 V. This value in hydrogen excess atmosphere could not be explained by thermal electric properties. This phenomenon may come from layered structure. This hypothesis suggests that the possibility of a new type fuel cell by using layered compounds for electrolyte.

$LaSr_3Fe_3O_{10}$ (LSFO) is n=3 ruddlesden-popper (RP) type perovskite oxide which has the layered structure.

The RP-type oxides exhibiting ion conduction, electronic conduction and catalysis are attractive for use in many electrochemical applications. For example, RP-type oxides are currently used as cathode material for solid oxide fuel cell (SOFC) [2]. Therefore, LSFO is characterized by electrochemical measurements in hydrogen excess atmosphere, and the carrier in LSFO is determined by measuring membrane potential for concentration cell of NaOH (pH 12 and pH 10).

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Experimental section

Preparation of single cell

LSFO samples were prepared by solid state reaction using powders of La_2O_3, $SrCO_3$ and Fe_2O_3. These precursors were weighted in stoichiometric proportions, and ball milled at 300 rpm for 30 min, followed by pressing in the form of bars. They were calcined in air at 1400ºC for 3 h [3]. The powder samples thus obtained were reground in an agate mortar. Finally, the powder samples were pressed into pellets and sintered in air at 900ºC for 10 h. The resulting pellets were cylinder shapes with 5 mm thick and 10 mm in diameter. Pd catalyst (15wt% Pd/LSFO) was prepared by impregnation method. For preparation of the Pd catalyst, 1.0 g of LSFO powder and 3.87 g of $Pd(NO_3)_3(NH_3)_2$ were added to an evaporating dish. The mixture was kept at 80ºC on water bath. After evaporating, the mixture was calcined in air at 600ºC for 2 h, and then ground. The Pd catalyst was dispersed in ethylene glycol and coated to one side of an electrolyte, then, calcined in air at 400ºC for 2 h.

This prepared powder was checked by using X-ray powder diffraction patterns collected with a Cu Kα X-ray source (40 kV, 20 mA).

Measurement of electrochemical property

For the measurement of cell voltage, the cells which were reduced in H_2 at 150°C for 2 h were mounted on a teflon specimen support (Figure 1). The measurement was carried out using a three-electrode cell. The Pt wire counter and reference electrode were put on both side pellet. The furnace temperature was set to ambient temperature. The cells were operated in the single-chamber flowing H_2-O_2-N_2 mixtures. The total flow rate of the gas mixture was fixed at 100 ml min^{-1} (H_2/ O_2/ N_2=37.1/ 3.2/ 59.7). The changes in the potential were measured for response as a function of time on stream with/without H_2 concentration. The flow rate of H_2 was switched from 37.1 ml min^{-1} to 0 ml min^{-1} and back to 37.1 ml min^{-1}.

We determined the charge carrier in $LaSr_3Fe_3O_{10}$ by measuring membrane potential for concentration cell of NaOH (pH 12 and pH 10). By comparison, we measured the membrane potential of AEM as an anion conducting membrane and Nafion as a proton conducting membrane.

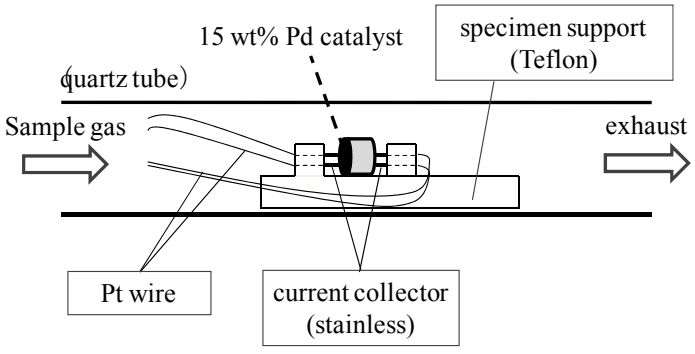

Figure 1. Schematic illustration of the apparatus.

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Results and Discussion

Figure 2 shows an XRD pattern of LSFO powder. The XRD shows that the product is perovskite oxide LSFO with a tetragonal structure (*I*4 / *mmm* space group), the diffraction date are in good agreement with JCPDS card of $LaS_3Fe_3O_{9.9}$ (JCPDS card no.01-081-1234). The peaks near 32º is attributed to [110] and a characteristic peak of n=3 RP-type perovskite.

A plot of the potential at room temperature as a function of time and stream with/ without H_2 is shown in Figure 3. The changes in the potential showed a quick response for the presence of H_2 at 25°C. The value of the voltage increased from 0 V to 0.9 V within about 3 min after flowing the H_2, and decreased from 0.9 V to 0 V within about 3 min after stopping the supply of H_2. Furthermore, the cell voltage reached about 0.9 V without cathode catalyst in the presence of H_2. The performance did not change after a number of times this cycle. The results suggested that the Pd/LSFO anode and LSFO cathode were selectively active for hydrogen reduction reaction and oxygen reduction reaction, respectively, since cathode was inert for activation of hydrogen. Oxygen reduction reaction proceed on oxide such as LSFO, since electro-kinetics of oxygen reduction reaction in an alkaline medium is much faster than that in an acidic medium as shown in the following equations [4]:

Anode (Pd/LSFO) : $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ $E_0 = -0.83$ V
Cathode (LSFO) : $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$ $E_0 = 0.40$ V

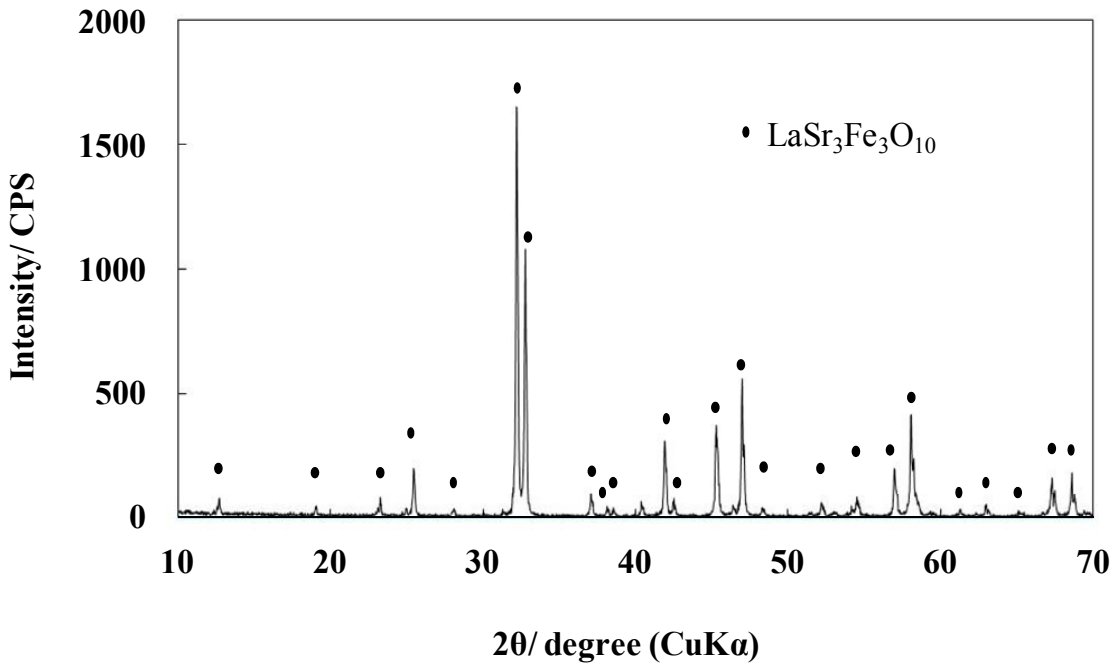

Figure 2. XRD pattern of LSFO powder.

We measured membrane potential for concentration cell of NaOH to determine the charge carrier. When KOH solution is used, same results were obtained. The membrane potential of AEM, Nafion, and $LaSr_3Fe_3O_{10}$ are shown in TABLE I. Nafion was pretreated with NaOH solution. When electrolyte shows anion conductivity, the membrane potential is -118 mV from equilibrium potential of Nernst's equation. On the

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other hand, when electrolyte shows only cation conductivity, the membrane potential is +118 mV. For AEM and Nafion, the membrane potential values were negative and positive, respectively. However, both AEM and Nafion were not in agreement with the theoretical value (-118, +118 mV). The results suggest that AEM and Nafion slightly showed cation and anion conductivity, respectively. The membrane potential of LSFO showed negative value. Therefore, the carrier in LSFO was OH^-. However, the membrane potential was not in agreement with the theoretical value and adding $NaNO_3$ into the pH 12 side with LSFO electrolyte, the membrane potential increased (TABLE II). This increase of the potential suggests that LSFO has some cation conductivity. These results suggest that LSFO has both anion and slightly cation conductivities. The main carrier of LSFO was OH^- because of showing negative value of the membrane potential adding $NaNO_3$. This OH^- can be attributed to the intercalation of water, since the oxygen-deficient n=3 Ruddlesden-Popper (RP) type oxides react with water at room temperature [5]. In fact, a peak at $2\theta=4.9^\circ$, 9.8° of the XRD pattern (Figure 4a) of the LSFO powder after fuel cell test shows that a new phase contains H_2O molecules and OH groups. Therefore, LSFO will be able to be used for a new anion-conducting fuel cell.

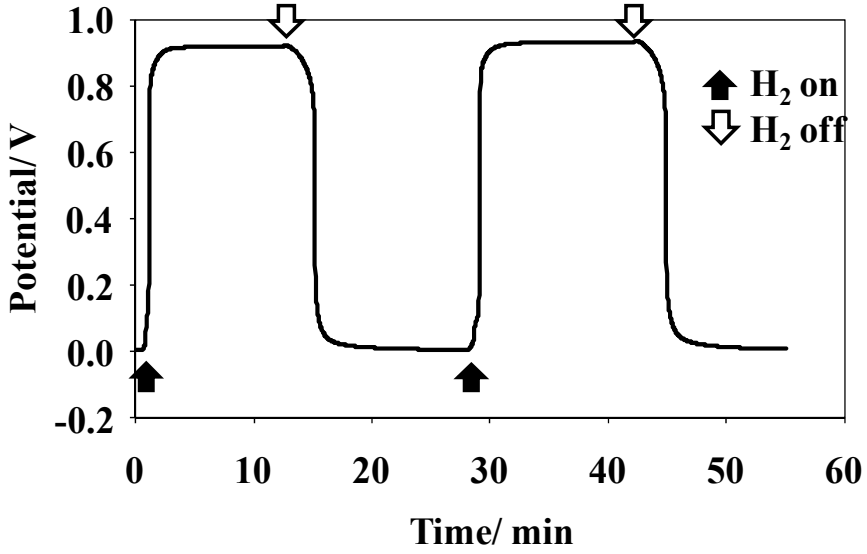

Figure 3. The changes in the potential of the cell consisting of LSFO at room temperature as a function of time and stream with/without H_2 concentration in the mixture gas ($H_2/O_2/N_2$ = 37.1/ 3.2/ 59.7 ml min^{-1})

TABLE I. Membrane potential using three kinds of electrolyte.

Electrolyte	Membrane potential/ mV
LSFO	-60.2
Nafion	89
AEM	-101

TABLE II. Dependence of potential on Na^+ concentration with LSFO electrolyte.

Solution	Membrane potential/ mV
NaOH (pH 10) and NaOH (pH 12)	-60.2
NaOH (pH 10) and NaOH (pH 12) + $NaNO_3$	-29.6

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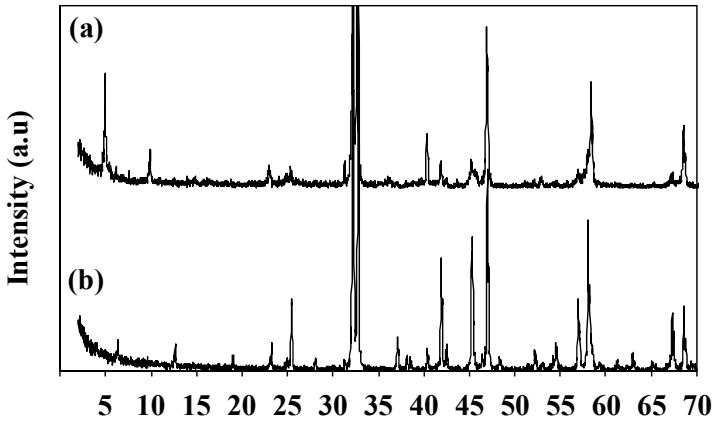

Figure 4. XRD patterns of (a) the LSFO powder after fuel cell test, (b) the as-prepared LSFO.

Conclusions

$LaSr_3Fe_3O_{10}$ electrolyte showed very high voltage without cathode catalyst in the presence of H_2. The results revealed characteristic property of AFC, and the carrier of LSFO was determined as OH^- by the membrane potential for concentration cell of NaOH. These results suggest that the possibility of a new type fuel cell by using LSFO as electrolyte.

Acknowledgments

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