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Performance of Solid Alkaline Fuel Cells Employing Layered Perovskite-Type Oxides as Electrolyte

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Layered perovskite-type oxides were characterized by electrochemical measurement. Five kinds of perovskite oxides ($LaSr_3Fe_3O_{10}$, $NaLaTiO_4$, $Sr_4Co_{1.6}Ti_{1.4}O_8(OH)_2 \cdot xH_2O$, $RbLaNb_2O_7$ and $LaFeO_3$) were used as electrolyte of fuel cells. Every perovskite oxide could generate current and high open circuit voltage (>0.8 V). The results were attributed to hydroxide ion (OH^-) conduction resulting from reduction and H_2O treatments. This hypothesis suggests that the possibility of a new alkaline fuel cell by using layered perovskite as electrolyte.

Introduction

The fuel cells are interesting electrochemical devices and environmentally friendly power devices because of their high energy-conversion efficiency and power density with no or low emissions. In recent years, alkaline fuel cell (AFC) has attracted increasing attention due to possibility of using non-precious metal catalyst. Because, it is well known that electro-kinetics of oxygen reduction reaction in an alkaline medium is much enhanced in comparison with an acid medium as shown in the following equations[1]:

Anode : $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$E_0 = -0.83$ V	(1)
Cathode : $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$	$E_0 = +0.40$ V	(2)
Overall : $H_2 + 1/2O_2 \rightarrow H_2O$	$E_0 = +1.23$ V	(3)

In addition, many materials show superior corrosion resistance in alkaline than in acid environments. These lead to use non-precious catalysts (*e.g.*, Ni, Ag, perovskite-type oxides, etc.). However, the thermal stability of AFC is very low, so that attention has recently been increasingly focused on inorganic electrolytes which are stable up to 150°C or higher.

In our previous works, n = 3 ruddlesden-popper member $LaSr_3Fe_3O_{10}$ (LSF) showed OH^- conductivity, and the single-chamber fuel cell with LSF electrolyte showed high voltage (0.9 V) without a cathode catalyst in the hydrogen rich mixture gas (H_2-O_2-N_2). This suggests that LSF can be used as electrolyte for a new type AFC.

In the present study, we examined performance of fuel cells with five kinds of perovskite oxides ($LaSr_3Fe_3O_{10}$, $NaLaTiO_4$, $Sr_4Co_{1.6}Ti_{1.4}O_8(OH)_2 \cdot xH_2O$, $RbLaNb_2O_7$

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and $LaFeO_3$) as electrolyte, and how the layered perovskite–type oxides have functions of OH^- conduction.

Experimental section

Preparation of single cells

The samples of $LaSr_3Fe_3O_{10}$ (LSF), $NaLaTiO_4$ (NLT), $Sr_4Co_{1.6}Ti_{1.4}O_8(OH)_2 \cdot xH_2O$ (SCT), $RbLaNb_2O_7$ (RLN) and $LaFeO_3$ (LFO) were synthesized by solid-state reaction from La_2O_3, $SrCO_3$ and Fe_2O_3; La_2O_3, TiO_2 and Na_2CO_3; $SrCO_3$, Co_3O_4 and TiO_2; La_2O_3, Rb_2CO_3 and Nb_2O_5; La_2O_3 and Fe_2O_3, respectively[2-6]. In the case of LSF, SCT and LFO preparation, these precursors were weighted in stoichiometric proportions, however, generally RLN and NLT preparation, 30% excess of Rb_2CO_3 and 50% excess of Na_2CO_3, respectively. These precursors were mixed by planetary ball mills at 300 rpm for 1 h, followed by pressing in the form of bars. They were calcined in air at various temperatures. The LSF, NLT, SCT, RLN, LFO were prepared by calcination at 1400ºC for 3 h, 900ºC for 30 h, 1275ºC for 24 h, 1100ºC for 3 h and 1400ºC for 4 h, respectively. The calcined NLT and RLN was washed thoroughly with distilled water to wash away the excess Na ions and Rb ions, and dried at 120ºC. 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 1 mm thick and 20 mm in diameter. Pd catalysts (15wt% Pd/perovskite oxides) were prepared by impregnation method. For preparation of the Pd catalyst, 1.0 g of perovskite oxide powder and 3.87 g of $Pd(NO_3)_2(NH_3)_2$ 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.

Measurement of electrochemical property

The anode (area = 0.28 cm^2) were attached on one side of the perovskite oxides electrolyte. Two gas chambers were set up by placing a cell between two pyrex tubes (Figure 1). Each chamber was sealed with an O-ring. Before fuel cell testing, the anode with a perovskite electrolyte was reduced in flowing hydrogen. The fuel and oxidant chambers were supplied with dry hydrogen and humidified oxygen, respectively, at flow rate of 20 ml min^{-1}. The voltage-current density curves were measured between 25 and 75°C.

The charge carrier in each perovskite oxides was determined by measuring membrane potential for concentration cell of NaOH (pH 12 and pH 10). Two NaOH solution chambers were set up by placing an electrolyte a between two glass tubes (Figure 2). Ag/Ag_2O electrodes were used as OH^--sensing electrode. To protect oxidation coat of electrodes, Ag_2O powder was added to each solution. By comparison, we measured the membrane potential of alkaline exchange membrane (AEM) as an anion-conducting membrane and Nafion as a cation conducting membrane.

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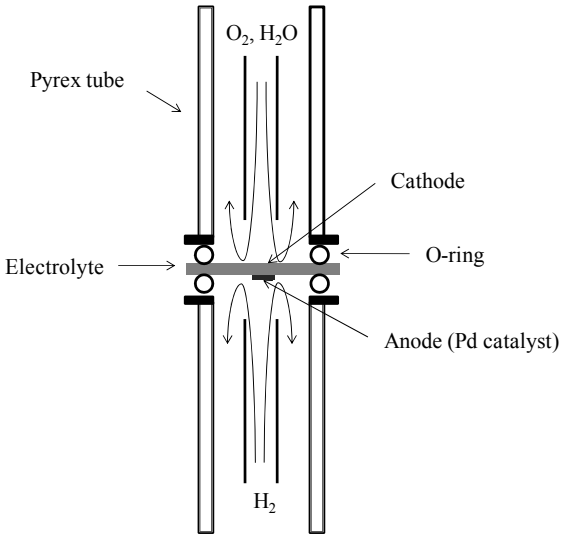

Figure 1. Schematic illustration of the electrochemical cell.

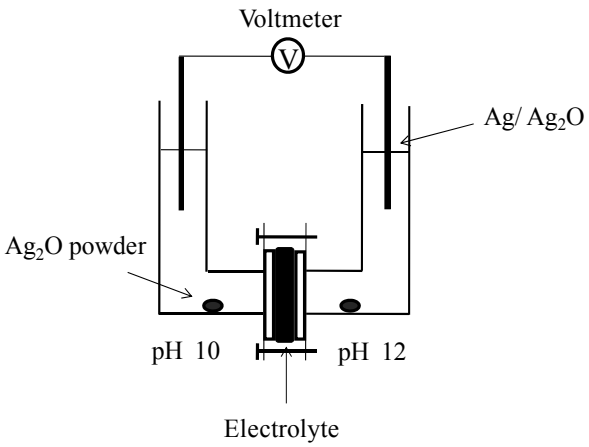

Figure 2. Schematic illustration of the concentration cell of NaOH.

Results and Discussion

Electrochemical performance.—Figure 3 shows the electrochemical performances of five kinds of perovskite oxides. Every cell generates current and exhibits high open circuit voltage (> 0.8 V) without cathode catalyst. These results represent the characteristic property of AFC and the first case of success of AFC with perovskite oxides as electrolytes. In particular, the RLN electrolyte shows the highest OCV (1.01 V), and the SCT electrolyte shows the highest current density (4.0 mA cm^{-2}) among the five kinds of electrolytes. The relative density of the RLN electrolyte may be higher than that of another electrolyte. We now consider the reason why the oxides show the OH^- conduction. The OH^- conduction 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[7], as follows.

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$$LaSr_3Fe_3O_{10} \xrightarrow{\text{Reduction}} LaSr_3Fe_3O_{10-\delta} \xrightarrow{H_2O\ \text{treatments}} LaSr_3Fe_3O_{10-2\delta}(OH)_{2\delta}\cdot\delta H_2O$$

The reduction treatments made the layered perovskite compounds oxygen deficiency, and the H_2O treatments led to a new phase containing H_2O and OH^-. This OH^- might be a charge carrier. The SCT electrolyte might have more OH^- carrier than other perovskite oxides, and showed the highest current density.

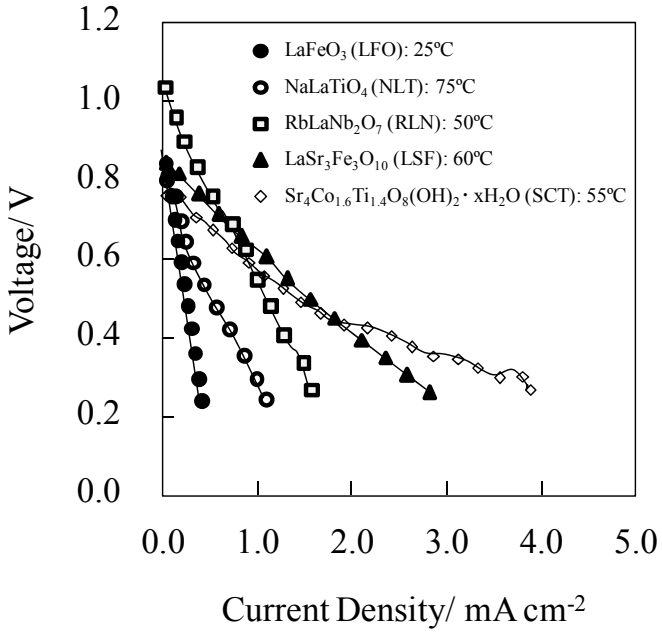

Figure 3. Comparison of the electrochemical performances of (●) LFO, (○) NLT, (■) RLN, (▲) LSF and (◇) SCT electrolyte under operating conditions with hydrogen flow rate of 20 ml min^{-1} and humidified oxygen flow rate of 20 ml min^{-1} (humidified at 45~95°C).

Charge carrier.—We measured membrane potential for concentration cell of NaOH to determine the charge carrier of five kinds of perovskite oxide. The membrane potential of AEM, Nafion, and five kinds of perovskite oxide are shown in TABLE I. The LFO electrolyte was very brittle, so we could not measure the membrane potential of LFO. When an electrolyte shows only anion conductivity, the membrane potential is -118 mV from equilibrium potential of Nernst's equation. On the other hand, when an electrolyte shows only cation conductivity, the membrane potential is +118 mV. For AEM and Nafion, the membrane potential values were -101 mV and +89 mV, respectively. However, both AEM and Nafion are not in agreement with the theoretical value (-118, +118 mV). The results suggest that AEM and Nafion slightly show cation and anion conductivity, respectively. The membrane potential of LSF, SCT and NLT shows negative value. Therefore, the main carriers in these perovskite oxides are OH^-. The membrane potential of RLN showed +5.3 mV. This result shows RLN is cation conductor. However, the fuel cell with the RLN electrolyte generated current and high voltage without cathode catalyst. We presume that the reduction treatment is the most important procedure. Therefore, we measured the membrane potential of the RLN electrolyte which was reduced at 300ºC for 2 h in hydrogen. The membrane potential of

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the reduced RLN showed -61.9 mV. This result might ensure the hypothesis of preparation of OH^- in perovskite oxides. From these results and the hypothesis, by using layered perovskite electrolytes, a new type AFC was successfully demonstrated.

TABLE I. Membrane potential using five kinds of electrolyte.

Electrolyte	Membrane potential/ mV
Nafion	+89
AEM	-101
LSF	-60.2
SCT	-66.8
NLT	- 36.3
RLN	+5.3
Reduced RLN	-61.9
LFO	Unmeasurable

Conclusions

The five kinds of layered perovskite oxides showed electrochemical performance as electrolyte for fuel cell without cathode catalyst. The results conformed to characteristic property of AFC. The OH^- as a charge carrier was formed in the layer from the reduction treatment and the H_2O treatment. This hypothesis suggests that the possibility of a new alkaline fuel cell by using layered perovskite as electrolyte.

Acknowledgments

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