EVALUATION OF LANTHANUM-CONCENTRATE FOR SOFC SEPARATOR

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ABSTRACT

This R&D has focused on reducing the cost of solid oxide fuel cell (SOFC) modules through the application of lanthanum-concentrate to the separator and/or the cathode. A database, which is described in this report, was created with respect to the solution limit, relative density, and thermal expansion behaviors of lanthanum chromite perovskite when light rare earth (Ln, Ln=Ce, Pr, Nd) elements were substituted for high-purity lanthanum, in order to examine the effects of various combinations of Ln elements on the separator. Most (La$_{1-y}$Ce$_y$)$_2$CrO$_3$ samples contained a small amount of impurities in addition to the perovskite phase. AE(AE=Ca, Sr) doping of La$_{1-x}$Ln$_x$CrO$_3$ (Ln=Ce, Pr, Nd) increased their TECs, whereas the rare earth metal-doping of La$_{1-y}$AE$_y$CrO$_3$ decreased its TEC.

INTRODUCTION

Solid oxide fuel cell (SOFC) is a very promising system with high efficiency. However there are still many materials problems. Recently, Itoh et al. has reported simulation and estimation results on the production cost of the stack segments in two types of SOFC, planar type and the tubular type (1). They reported that significant material costs were accounted from the expensive high-purity La$_2$O$_3$, especially in the case of cathode-supported tubular type SOFC where the major portion of the cell materials is the lanthanum manganite cathode (LaMnO$_3$), and in the case of planar type SOFC is the lanthanum chromite separator (LaCrO$_3$). To reduce the materials cost without degrading their characteristics, separator and cathode materials prepared by cheaper La-based raw materials are a significant attractive.

Many kinds of rare earth (RE) elements exist in the RE-mineral together, and they are separated into 3 groups in atomic weight order. La is belonged in the lightest atomic weight group which consist of La, Ce, Pr and Nd(light rare earth=Ln). Thus, we have focused on the synthesis of LnCrO$_3$ and LnMnO$_3$ perovskite using cheapest La-based concentrate with Ce, Pr and Nd instead of expensive La element of high-purity.
In this study, LaCrO$_3$ perovskites were made by using light rare earth elements (Ln=Ce, Pr or Nd) and investigated for possible use in SOFC separator.

**EXPERIMENTAL**

(La$_{1-x}$RE$_x$)$_{1-y}$AE$_y$CrO$_3$ (0 $\leq$ x $\leq$ 0.3, 0 $\leq$ x $\leq$ 0.5) powders were synthesized using ordinary ceramic method with 19 samples and basic composition powders being prepared by the Pechini method in order to confirm and improve the reliability of the data. Starting material powders, La$_2$O$_3$ (pre-heated at 1500 °C for 3 h), SrCO$_3$, CaCO$_3$, Cr$_2$O$_3$, CeO$_2$, Pr$_2$O$_3$ and Nd$_2$O$_3$ were mixed in the Al$_2$O$_3$ mortar. After being mixed, the mixtures were heated at 1200 °C for 10 h in air. The milling and heating procedures were repeated twice. The powders were pressed into pellets with 40 mm in diameter under 40 MPa. The pellets were finally sintered in air at 1600 °C for 20 h and cut into a rectangular shape of 3.5 mm $\times$ 3.5 mm $\times$ 20 mm. All the sample phases were confirmed by X-ray diffractometry (JEOL JDX8030). Average thermal expansion coefficient (TEC) was measured by using Mac Science TD-5000S equipment in the temperature range 50-1000 °C. References used for the TEC measurements were a rod of sapphire in air and in H$_2$ atmosphere. The heating rate was 4 °C min$^{-1}$ in air and H$_2$ atmosphere. A flow rate of 100 ml min$^{-1}$ of H$_2$ gas was used during these measurement after it had been bubbled through pure water at 20 °C.

**RESULT AND DISCUSSION**

**Solution Limit of Individual Light Rare Earth Elements**

Table 1 shows crystal structures and relative densities of (La$_{1-x}$Ln$_x$)$_{1-y}$AE$_y$CrO$_3$ (Ln=Ce, Pr, Nd, AE=Sr, Ca). All samples for powder X-ray diffraction (XRD) analysis were prepared with pulverization after being fired at 1,600°C for 20 hours. The results from the XRD analysis suggest the following points:

1. In the case of Ce-doped lanthanum chromites, samples can be made with a Ce-content of less than 6 mole%.
2. The Pr and Nd dopant dissolved in lanthanum chromite for all the compositions, and mostly formed orthorhombic crystal structures.
3. The crystal structure of all the samples changes from orthorhombic to rhombohedral with increasing Sr-contents, but the Ca-doped samples show orthorhombic structure, irrespective of the species of Ln-dopant.

Theoretical and relative densities of the samples were also calculated from the results of the XRD analysis. The data shows that the density increases with increases in the
content of Sr or Ca, and that density is improved by Ln-doping in the order Pr\(\geq\)Nd\(\geq\)Ce.

These results say that the Ce dopant is not easy to dissolve in lanthanum chromite. On the other hand, Ca-doped lanthanum chromites are possible to prepare Ln-doped samples easily. Lanthanum chromites of basic composition prepared by the Pechini method was a good agreement with results of same composition samples by synthesized using ordinary ceramic method.

**Thermal Expansion Behaviors of \((La_{1-x}Ln_x)_{1-y}AE_yCrO_3\)**

The thermal expansion behavior of the samples, which were free from impurities, was observed under an oxidizing or a reducing atmosphere from 50 to 1,000°C. Table 2 shows the TECs of \((La_{1-x}Ln_x)_{1-y}AE_yCrO_3\) (Ln=Ce, Pr, Nd, AE=Sr, Ca) in air and the H\(_2\) atmosphere. The average linear thermal expansion coefficient (TEC) for the samples was calculated, and anomalous thermal expansions for the phase transformation (AEPT) and the oxygen defect (AEOD) were analyzed. The results from these analyses show that:

1. TECs increase with increasing AE content under each atmosphere, and in particular the values for Ca-doped materials were greater than for Sr-doped samples. (Fig.1)
2. Under the oxidizing atmosphere, TECs decrease with increasing Ln-contents due to an A-site effect.
3. AEPT shifts to higher temperature ranges with increasing Ca-contents, but to lower temperature ranges with increasing Sr-contents.
4. AEOD occurs in almost all the samples, and increasing the Sr- or Ca-contents makes this clearer.
5. The anomalous expansion shifts to higher temperature regions with increasing RE-contents.
6. Composition regions without AEPT are lower Ln and higher Sr, or higher Ln and lower Ca.

**CONCLUSIONS**

The possibility of using lanthanum concentrate chromite for SOFC separator has been investigated by the use of AE-doped lanthanum chromites with light rare earth metals, Ce, Pr, or Nd. The control of Ln-composition, especially Ce is necessary for use in the lanthanum chromite separator. Furthermore, it is necessary to investigate a sinterability method to get high relative density without gas leak.
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Fig. 1 Average linear TECs of the \((La_{0.5}Ln_{0.5})_{1-x}AE_xCrO_3\) as a function of AE content from 50 to 1000 °C in air and the H_2 atmosphere. (a);Ln=Ce, (b);Ln=Pr, (c);Ln=Nd

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Electrochemical Society Proceedings Volume 99-19

719
Table 1  Crystal structures and relative densities of (La$_{1-x}$Ln$_x$)$_{1-y}$AE$_y$CrO$_3$
(Ln=Ce, Pr, Nd, AE=Sr, Ca)

(1) La$_{1-x}$AE$_x$CrO$_3$

|        | 0    | 0.1  | 0.2  | 0.3  |
|--------|------|------|------|------|
| Sr     | OR(58.4) | OR(61.0) | OR(59.7) | OR(63.6) |
| Ca     | O(59.2) | O(62.1) | O(64.3) |       |

(2) (La$_{1-x}$Ce$_x$)$_{1-y}$AE$_y$CrO$_3$

|        | 0.02 | 0.04 | 0.06 | 0.08 | 0.10 |
|--------|------|------|------|------|------|
| Sr=0.1 | OR(53.6) | OR(55.0) | Cr$_2$O$_3$ | Cr$_2$O$_3$ | O(54.1) |
| Sr=0.2 | OR(58.4) | OR(59.2) | Cr$_2$O$_3$ | O(56.9) | O(56.2) |
| Sr=0.3 | OR(61.3) | OR(61.4) | Cr$_2$O$_3$ | OR(60.6) | OR(57.8) |
| Ca=0.1 | OR(57.8) | OR(56.7) | OR(54.9) | O(54.9) | O(54.0) |
| Ca=0.2 | OR(60.0) | OR(59.4) | OR(58.0) | O(55.9) | O(55.8) |
| Ca=0.3 | OR(61.3) | OR(62.1) | OR(58.5) | OR(55.7) | OR(56.0) |

(3) (La$_{1-x}$Pr$_x$)$_{1-y}$AE$_y$CrO$_3$

|        | 0.1  | 0.2  | 0.3  | 0.4  | 0.5  |
|--------|------|------|------|------|------|
| Sr=0.1 | OR(58.7) | OR(56.4) | OR(56.2) | OR(56.3) | OR(55.8) |
| Sr=0.2 | OR(58.7) | OR(60.1) | OR(59.1) | OR(58.3) | OR(59.6) |
| Sr=0.3 | OR(62.3) | OR(61.5) | OR(61.3) | OR(60.4) | OR(61.7) |
| Ca=0.1 | OR(59.4) | OR(59.3) | OR(58.5) | OR(59.3) | OR(58.0) |
| Ca=0.2 | OR(61.8) | OR(62.7) | OR(61.1) | OR(60.0) | OR(64.2) |
| Ca=0.3 | OR(64.7) | OR(65.8) | OR(63.7) | OR(62.3) | OR(70.4) |

(4) (La$_{1-x}$Nd$_x$)$_{1-y}$AE$_y$CrO$_3$

|        | 0.1  | 0.2  | 0.3  | 0.4  | 0.5  |
|--------|------|------|------|------|------|
| Sr=0.1 | OR(67.5) | OR(59.2) | OR(57.8) | OR(57.4) | OR(56.1) |
| Sr=0.2 | OR(60.6) | OR(59.2) | OR(58.8) | OR(56.2) | OR(56.1) |
| Sr=0.3 | OR(62.7) | OR(60.2) | OR(59.4) | OR(58.5) | OR(76.3) |
| Ca=0.1 | OR(63.3) | OR(64.4) | OR(62.3) | OR(62.2) | OR(61.1) |
| Ca=0.2 | OR(59.1) | OR(58.8) | OR(57.8) | OR(57.7) | OR(57.6) |
| Ca=0.3 | OR(61.2) | OR(60.6) | OR(59.9) | OR(61.3) | OR(60.7) |

*1: The symbols used in this table are “O” for Orthorhombic, “R” for Rhombohedral,
“OR” for Orthorhombic +Rhombohedral, respectively.
*2: Values in parenthesis are for the relative density (%).
*3: Gray cells in this table represent materials in which impurities were detected, with
the composition being given.

720 Electrochemical Society Proceedings Volume 99-19
Table 2  TEC of (La$_{1-x}$Ln$_x$)$_{1-y}$AE$_y$CrO$_3$ (Ln=Ce,Pr,Nd, AE=Sr,Ca) in air and the H$_2$ atmosphere.

|      | (1)La$_{1-x}$Sr$_x$AE$_y$CrO$_3$ | (2)La$_{1-x}$Ce$_x$AE$_y$CrO$_3$ | (3)La$_{1-x}$Pr$_x$AE$_y$CrO$_3$ | (4)La$_{1-x}$Nd$_x$AE$_y$CrO$_3$ |
|------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
|      | y=0                             | y=0.02                          | y=0.1                           | y=0.1                           |
|      | 8.5(8.6)                        | 8.4(8.6)                        | 9.0(9.9)                        | 8.3(8.5)                        |
|      | Sr=0.1                          | Sr=0.2                          | Sr=0.1                          | Sr=0.2                          |
|      | 9.4(10.4)                       | 10.2(12.6)                      | 9.9(10.0)                       | 10.4(14.6)                      |
|      | Ca=0.1                          | Ca=0.2                          | Ca=0.1                          | Ca=0.2                          |
|      | 9.1(10.0)                       | 9.5(11.8)                       | 9.9(14.8)                       | 10.1(14.2)                      |
|      | Ca=0.3                          | Ca=0.2                          | Ca=0.3                          | Ca=0.3                          |
|      | 9.7(12.3)                       | 9.9(15.2)                       | 10.0(21.1)                      | 10.1(16.1)                      |

* : Values outside the parenthesis represent the thermal expansion coefficient ($\times 10^{-6}$ /°C) in air, while those in the parenthesis represent this coefficient in the reduction atmosphere. Shaded background values represent samples without anomalous expansion for the phase transformation or oxygen defect. Cells without values represent compositions which were possible to prepare.