Solid State Reaction of $\text{La}(\text{Co}_{1-x}\text{Ni}_x)\text{O}_3$ with 10 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$

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The reaction of cubic ZrO_2 with $\text{La}(\text{Co}_{1-x}\text{Ni}_x)\text{O}_3$ was investigated by hot pressing at 1573 K. The reaction can be seen for all of x . The compositions of the reacted areas were estimated as $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{La}_2\text{Zr}(\text{Ni}_{0.6}\text{Co}_{0.4})\text{O}_6$ and $\text{La}_2\text{ZrNiO}_6$ for $x=0, 0.4$ and 1 , respectively. The width of the reacted area decreased with increasing Ni fraction. The sintering of samples with compositions of the reacted areas mentioned above was made to investigate the crystal structures, electric resistivities and thermal expansion coefficients of the reacted compounds. The thermal expansion coefficients of the reacted compounds were always intermediate between those of cubic ZrO_2 and $\text{La}(\text{Co}_{1-x}\text{Ni}_x)\text{O}_3$. The electric resistivity of $\text{La}_2\text{Zr}_2\text{O}_7$ was an extremely high order of $10^3 \Omega \cdot \text{m}$ even at the temperature of 1273 K. The substitution of Ni or Co for the Zr site decreases the electric resistivity and becomes the order of $10^{-1} \Omega \cdot \text{m}$ at the temperature of 1273 K. The electrode materials of cubic ZrO_2 fuel cells are also discussed on the basis of the present experimental results.

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I. Introduction

The cubic ZrO_2 with 8–10 mol% Y_2O_3 is used for the high-temperature solid fuel cell because of its high ionic conductivity⁽¹⁾. Platinum is considered as the electrode for fuel cell which is stable at high temperatures in the air atmosphere. Since Pt is expensive and become unstable above 1100 K, the development of electrode materials which can be used at high temperatures above 1273 K is desired. The perovskite-type oxide LaCoO_3 is one of the candidates for the electrode materials because of its high electrical conductivity at room temperature⁽²⁾⁽³⁾. However, LaCoO_3 is not appropriate for the electrode of cubic ZrO_2 . The first reason is that it has larger thermal expansion coefficients than cubic ZrO_2 . The second is that it reacts with cubic ZrO_2 and then forms $\text{La}_2\text{Zr}_2\text{O}_7$, which is almost insulator, at the interface^{(4)–(6)}. In general, the physical properties of the perovskite ABO_3 compound can be design-

ed by the substitution of other elements for A or B sites without any change of fundamental crystal structure⁽⁷⁾. The present work was aimed to obtain the material with a thermal expansion coefficient comparable to cubic ZrO_2 by substitution of Ni atoms for Co sites in LaCoO_3 .

The authors aimed to investigate the reaction of 10 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ with $\text{La}(\text{Co}_{1-x}\text{Ni}_x)\text{O}_3$ by hot pressing in air. We also examined the crystal structures, thermal expansion coefficients and electrical properties of the reacted products formed by the bonding of $\text{La}(\text{Co}_{1-x}\text{Ni}_x)\text{O}_3$ with 10 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ as well as of $\text{La}(\text{Co}_{1-x}\text{Ni}_x)\text{O}_3$ itself.

II. Experimental Details

The starting materials were La_2O_3 (99.99%), Co (99.9%) and Ni (99.99%) powders. The powders of $\text{La}(\text{Co}_{1-x}\text{Ni}_x)\text{O}_3$ ($x=0, 0.2, 0.4, 0.6, 0.8$ and 1) (termed LCNO hereafter) were mixed and then pressed into rods. The rods were sintered at 1573 K for 86 ks in air⁽⁸⁾. The sintered rod was cut into several pieces for X-ray diffraction, measurements of electrical resistivity and thermal expansion coefficients, and transmission electron microscopy (TEM).

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Thin foils for TEM were obtained by ion milling after mechanical polishing.

The single crystal of 10 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (c-ZrO₂) was cut and polished on the (100) plane. The bonding of LCNO with c-ZrO₂ was performed by hot-pressing on the sample of LCNO/(100)c-ZrO₂/LCNO, in sequence, at

1473 and 1573 K for 86 k–345.6 ks under the load of 2 MPa in air. The electrical resistivity was measured by the two-point method from room temperature to 1273 K in air.

The reaction at the interface after bonding was analyzed using an electron probe micro-analyzer (EPMA). TEM equipped with the

Fig. 1 X-ray powder diffraction of $\text{La}(\text{Co}_{1-x}\text{Ni}_x)\text{O}_3$ for $x = 0.2, 0.4, 0.6, 0.8$ and 1 .

energy dispersive X-ray spectroscopy (EDS) (Hitachi H-800) was used for the observation of the microstructures and the identification of the reacted phases.

III. Experimental Results

1. Synthesis and crystal structure of $\text{La}(\text{Co}_{1-x}\text{Ni}_x)\text{O}_3$

We have already reported the synthesizing condition of LaCoO_3 ⁽⁸⁾. It has been known that the reaction to LaCoO_3 from mixed powders of La_2O_3 and Co is completed by sintering at the temperature of 1573 K for 86 ks. We used the same sintering condition for the synthesis of LCNO. Figure 1 shows the results of X-ray powder diffraction for $x=0.2, 0.4, 0.6, 0.8$ and 1 of LCNO. The rhombohedral structure was kept up to $x=0.4$. On the other hand, the crystal structure of $x=0.8$ was different from the rhombohedral one and can be explained as being orthorhombic. The lattice parameter of $\text{La}(\text{Co}_{0.2}\text{Ni}_{0.8})\text{O}_3$ determined from X-ray diffraction was $a=0.566$ nm, $b=0.541$ nm and $c=2.789$ nm. At the composition of $x=0.6$, both of the rhombohedral and orthorhombic phases were identified. LaNiO_3 was unstable and decomposed into two phases of La_2NiO_4 and NiO by sintering at 1573 K for 86 ks, as reported by Odier *et al.*⁽⁹⁾

2. Electrical resistivity

Figure 2 shows the temperature dependence of electrical resistivity of LCNO from 300 to 1273 K. The resistivity of all samples decreases with the increase of temperature up to 673 K, which shows the semiconducting behavior. Above 673 K, the resistivity increases with the increase of temperature, which shows the metallic conduction. The composition dependence of resistivity at 1273 K indicates the minimum resistivity at $x=0.4$ of order of 10^{-3} $\Omega\cdot\text{m}$, as shown in Fig. 3.

3. Thermal expansion coefficients

Figure 4 shows the temperature dependence of linear thermal expansion of LCNO as well as c- ZrO_2 . The thermal expansion changes almost linearly with temperature. The thermal

Fig. 2 Temperature dependence of electric resistivity of LCNO.

Fig. 3 Composition dependence of electric resistivity of LCNO.

Fig. 4 Temperature dependence of linear thermal expansion of LCNO.

Fig. 5 Composition dependence of thermal expansion coefficients of LCNO.

expansion coefficients of c-ZrO₂ was $11 \times 10^{-6} \text{ K}^{-1}$, which is in good agreement with other work⁽¹⁰⁾. The thermal expansion coefficients of LCNO are shown in Fig. 5 as the function of Ni fraction of x . As the Ni fraction increases, the thermal expansion coefficients of LCNO decrease from $22 \times 10^{-6} \text{ K}^{-1}$ of LaCoO₃ to $13.4 \times 10^{-6} \text{ K}^{-1}$ of La₂NiO₄+NiO. The ther-

Fig. 6 Electron micrograph of LaCoO₃-ZrO₂ interface (a) and line analysis of composition across the interface by EPMA (b) bonded at 1573 K for 173 ks. Arrows indicate cracks. LC, R and Z indicate LaCoO₃, reacted zone and cubic ZrO₂, respectively. (c) bonded at 1573 K for 345 ks.

mal expansion coefficients of LCNO become closer to c-ZrO₂ with increasing Ni fraction.

4. Interface microstructures

The bonding of LCNO with the (100)c-ZrO₂ single crystal was carried out for $x=0, 0.4, 0.8$ and 1 of LCNO. The bonding of LaCoO₃ was difficult even under the hot pressing of 2 MPa at 1273–1573 K for 172.8 ks, which may be due to the large difference of the thermal expansion coefficients between LaCoO₃ and c-ZrO₂. Figure 6 shows the electron micrograph of an interface taken from one of the samples bonded at 1573 K. The cracks were observed near the interface. The reaction between LaCoO₃ and c-ZrO₂ can be seen by the line analysis of EPMA shown in Fig. 6(b). As the hot pressing interval was longer, the reacted zone became thicker as shown in Fig. 6(c). The line profile of EPMA reveals that the reacted zone at the

interface consists of La and Zr and the ratio of La to Zr is 1, so that the compound at the interface should be La₂Zr₂O₇. The Co and Y atoms are enriched at the LaCoO₃ and c-ZrO₂ side accompanied by the growth of La₂Zr₂O₇, respectively. The formation of La₂Zr₂O₇ at the interface also induced the two-phase region of LaCoO₃+CoO at the LaCoO₃ side⁽⁸⁾. The La₂Zr₂O₇ phase has already been reported as the reaction phase of LaCoO₃ with c-ZrO₂⁽⁴⁾⁽⁵⁾. Figure 7 shows the electron micrograph of the interface between c-ZrO₂ and La₂Zr₂O₇. The dislocations can be seen near the interface of c-ZrO₂. The electron diffraction patterns of c-ZrO₂ and La₂Zr₂O₇ reveal that the orientation relationship between them is the cube/cube relation, that is, $\{hkl\} // \{hkl\}$. It should be noted that the lattice parameter of La₂Zr₂O₇ is almost twice that of c-ZrO₂ and the misfit between them is about 5.8%.

Fig. 7 Electron micrograph of LaCoO₃/c-ZrO₂ interface (a) and electron diffraction patterns taken from c-ZrO₂ (b) and La₂Zr₂O₇ (c). Dotted line and arrows indicate the interface and dislocations, respectively.

Figure 8 shows the electron micrograph of the interface between LCNO of $x=0.4$ and c-ZrO₂ hot pressed at 1573 K for 172.8 ks at 2

Fig. 8 Electron micrograph of LCNO($x=0.4$)/c-ZrO₂ interface (a) and line analysis of composition across the interface by EPMA (b) bonded at 1573 K for 173 ks. LCN: La(Co_{0.6}Ni_{0.4})O₃, R: reacted zone, Z: c-ZrO₂.

MPa. There are no cracks at the interface. The compound can be found at the interface by the line analysis of EPMA and contains Co and Ni as well as La and Zr. The composition can be estimated from the flat area of X-ray intensity of EPMA as La:Zr:Ni:Co=2:1:0.6:0.4, that is, the compound of La₂Zr(Ni_{0.6}Co_{0.4})O₆. Figure 9 shows the bright field image of TEM taken from the interface of LCNO ($x=0.4$)/c-ZrO₂ hot pressed at the temperature of 573 K for 172.8 ks. The reacted area at the interface was made up of 1–2 μm grains. The electron diffraction patterns and EDS analysis reveal that each grain has a different chemical composition and crystal structure. This is shown in Fig. 9 by the symbols LZ, LZN and N, which indicate La₂Zr₂O₇, La₂Zr(Ni_{0.6}Co_{0.4})O₆ and NiO, respectively. However, the reason why the reacted zone consists of two or three compounds could not be made clear by the present experiment.

The bonded structure of La₂NiO₄+NiO with c-ZrO₂ is shown in Fig. 10 as hot pressed at 1573 K for 172.8 ks. The bonding seemed to be good and cracks were not seen at the interface. The composition of reacted area at the interface was the ratio of La:Zr:Ni=2:1:1 estimated from EPMA measurements, that is, La₂ZrNiO₆.

Figure 11 shows the thickness of the reacted area at the interface of LCNO/c-ZrO₂ bonded under the same condition of 1573 K for 172.8

Fig. 9 Electron micrograph of the interface between LCNO ($x=0.4$) and c-ZrO₂ showing the reacted area bonded at 1573 K for 173 ks. Z: 10 mol% Y₂O₃-ZrO₂, LZ: La₂Zr₂O₇, LZNC: La₂Zr(Ni_{0.6}Co_{0.4})O₆, N: NiO(CoO), LCN: La(Co_{1-x}Ni_x)O₃.

Fig. 10 Electron micrograph of the $(\text{La}_2\text{NiO}_4 + \text{NiO})/\text{c-ZrO}_2$ interface (a) and line analysis of composition across the interface by EPMA (b) bonded at 1573 K for 173 ks. LN: $(\text{La}_2\text{NiO}_4 + \text{NiO})$, Z: cubic ZrO_2 .

Fig. 11 Composition dependence of width of the reacted area between LCNO and c-ZrO_2 after hot-pressing at 1573 K for 173 ks.

ks for the fraction of Ni of LCNO. The thickness of the reacted area decreased with the increase in Ni fraction. It should be noted that the decrease of the reacted width with the increase of the Ni fraction is the same tendency of the thermal expansion coefficients difference

between LCNO and c-ZrO_2 with Ni fraction, which also decreases with Ni fraction. This fact suggests the possibility of the designing of the reacted zone thickness by the control of thermal expansion coefficients of electrode.

5. Properties of reacted products

As mentioned above, the reacted compounds at the interface were formed by the bonding of LCNO with c-ZrO_2 . Since the reacted compounds affect the electrical property of contact resistivity, it is important to know their properties. We investigated the structures, electrical resistivities and thermal expansion coefficients of these reacted compounds. The compositions prepared here were $\text{La}_2\text{Zr}_2\text{O}_7$ (LZO), $\text{La}_2\text{Zr}(\text{Ni}_{0.6}\text{Co}_{0.4})\text{O}_6$ (LZNCO) and $\text{La}_2\text{ZrNiO}_6$ (LZNO). The sintering condition of 1573 K for 172.8 ks was the same as that of bonding.

(1) Structures

Figure 12 shows the results of X-ray powder diffraction of LZO, LZNCO and LZNO, respectively. LZO is a cubic structure having the lattice constant of 1.079 nm. The lattice parameter obtained in the present experiment was in good agreement with the other work⁽¹¹⁾. On the other hand, there are no reports on the crystal structures of LZNCO and LZNO. The X-ray diffraction reveals that LZNO sintered at the temperature of 1573 K for 172.8 ks consists of three phases of LZNO, LZO and NiO. In the case of LZNCO, the sintered rod also consisted of three phases of LZNCO, LZO and NiO(CoO). These results were coincident with the structure observed by electron microscopy. Figure 13 shows the electron micrograph and electron diffraction patterns taken from the c-ZrO_2 side interface of the same area shown in Fig. 9. A and B indicate c-ZrO_2 and LZNCO, respectively. The orientation relationship between them is $(011)\text{Z} \parallel (101)\text{LZNCO}$ and $[111]\text{Z} \parallel [111]\text{LZNCO}$.

The crystal structure of LZNO was determined from the powder X-ray diffraction and the electron diffraction patterns shown in Fig. 14 to be orthorhombic with $a=0.4038$ nm, $b=0.411$ nm and $c=0.809$ nm. The crystal structure of LZNCO was also determined as

Fig. 12 X-ray powder diffraction of reacted products sintered at 1573 K for 173 ks. (a), (b) and (c) indicate samples of LZO, LZNCO and LZNO, respectively.

the orthorhombic structure of $a=0.4013$ nm, $b=0.411$ nm and $c=0.817$ nm.

(2) Electrical resistivity

The electrical resistivity was measured by the

two-point method from room temperature to 1273 K for the sintered rods of LZO, LZNCO and LZNO. Figure 15 shows the temperature dependence of electrical resistivity. The resistivity decreasing with temperature was observed

Fig. 13 Electron micrograph (a) and diffraction patterns taken from c-ZrO₂ (b) and LZNCO (c) bonded at 1573 K for 173 ks. This is the same area at the c-ZrO₂ side in Fig. 9.

Fig. 14 Electron diffraction patterns taken from a grain of LZNO. The beam direction was [010] (a) and [110] (b).

for all samples. At the temperature of 1273 K, the resistivity of LZO was very high and was $4 \times 10^3 \Omega \cdot \text{m}$; thus, the formation of LZO by reaction is not desirable for the electrode. On

the other hand, the substitution of Ni leads to the lower resistivity. The resistivity of LZNCO was $0.7 \Omega \cdot \text{m}$ at 1273 K, which is 10^4 times lower than that of LZO.

(3) Thermal expansion coefficients

Figure 16 shows the linear thermal expansion rate related with the temperature of the sintered samples composed of LZO, LZNO and LZNCO. The thermal expansion coefficients of LZO, LZNO and LZNCO obtained from Fig. 16 were $10.2 \times 10^{-6} \text{ K}^{-1}$, $11.6 \times 10^{-6} \text{ K}^{-1}$ and $13.4 \times 10^{-6} \text{ K}^{-1}$, respectively. These values of the reacted products were always intermediate between those of c-ZrO₂ and LCNO. This fact suggests that the reacted products play a role in the accommodation of the thermal expansion difference be-

Fig. 15 Temperature dependence of electric resistivities in sintered rods of LZO, LZNCO and LZNO.

Fig. 16 Temperature dependence of linear thermal expansion rate in sintered rods of LZO, LZNCO and LZNO.

tween them. This is also coincident with that the width of the reacted area becomes thinner as the thermal expansion difference becomes smaller.

IV. Discussion

The bonding of LaCoO_3 with 10 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ formed the reacted phase of $\text{La}_2\text{Zr}_2\text{O}_7$. The thermal expansion coefficients of LZO was very close to that of c- ZrO_2 . The lattice mismatch between them was about 5.8%, which gives good fitting of atoms at the interface. However, LZO shows such an extremely high resistivity that the formation of LZO induces the degradation of the electrode property.

The effect of the substitution of nickel for cobalt in LaCoO_3 was twofold. One was the thermal expansion coefficients, which decreased with increasing nickel fraction and became closer to that of c- ZrO_2 . The thickness of the reacted area also decreased the increase of the nickel fraction in the same manner. The other was the electric resistivity. The substitution of nickel for cobalt in LaCoO_3 leads to the reduction in electric resistivity of the reacted compounds by way of the formation of $\text{La}_2\text{Zr}(\text{Ni}_{0.6}\text{Co}_{0.4})\text{O}_6$. The existence of nickel and cobalt in LZNCO may change the conduction mechanism of LZO to that of $\text{LaCoO}_3^{(2)(3)}$.

These results seem to indicate the direction of the material design of the La-perovskite electrode for c- ZrO_2 fuel cell, that is,

- (1) to coincide the thermal expansion coefficients of the electrode with c- ZrO_2 , and
- (2) to add or substitute the perovskite for the valence-fluctuated elements such as Co, Ni, etc. to reduce the resistivity of the reacted phases.

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