SMOOTH CONNECTION BETWEEN SEPARATOR AND CATHODE USING GRADED STRUCTURES

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ABSTRACT

In order to decrease the contact resistance between La₀.₉Sr₀.₁CrO₃ separator and La₀.₉Sr₀.₁MnO₃ cathode, a graded structure was introduced between them. The starting powders were prepared by ultrasonic spray pyrolysis of aqueous solutions. By co-firing the laminated (La,Sr)CrₓMnO₃ (graded from x=0 to 1) powder sheets, disks with good connection were formed. Moreover, the thermal expansion mismatch between the separator and electrodes was decreased.

INTRODUCTION

In a planar SOFC, the separator has direct contact with each electrode. One of the problems in stacking SOFCs is a voltage drop due to the large contact resistance and low current collection efficiency at the interface between electrode and separator. A good electrical connection and chemical stability of these materials at high temperatures is necessary in order to obtain a high performance SOFC stack.

The compounds belonging to the LaCrO₃ system, used as the separator in SOFC systems are known to be hard to sinter and non-reactive to the Ni-zirconia cermet anode and LaMnO₃ based cathode even at high temperatures. Therefore, the contact between electrodes (anode and cathode) and separator becomes a serious problem. The most part of the voltage drop due to the contact resistance comes from the fuel electrode side. By inserting a thin Ni-doped lanthanum chromite, (La,Sr)Cr₁ₓNiₓO₃, sheet between the separator (LaCrO₃ based) and the fuel electrode (Ni-cermet), the contact resistance was suppressed and high current collection efficiency was obtained (1). Although the contact resistance between cathode and separator is smaller than that between fuel electrode and separator, it remains as one of the reason for the voltage drop in planar SOFC systems. Moreover, the mismatch of the thermal expansion rate of both sides (the T.E.C. of La₁ₓSrₓCrO₃ is around 9.5x10⁻⁶ (2) and that of La₁ₓSrₓMnO₃ is over 10x10⁻⁶(3)) also causes a decrease in current collection efficiency.

In this paper, introduction of a graded structure between (La,Sr)CrO₃ separator
and (La,Sr)MnO₃ cathode is proposed in order to realize good connection and decrease the contact resistance between them.

**EXPERIMENTAL**

La₀₉Sr₀ jCr, xMnxO₃ (x=0, 0.2, 0.4, 0.6, 0.8, 1.0), La₀₈Sr₀₂CrO₃ and La₀₈Sr₀₂MnO₃ powders were prepared by spray pyrolysis method(4). The aqueous solution dissolving each metal nitrate in the corresponding ratio was vaporized to spray state by ultrasonic oscillation, which was led into a furnace and pyrolyzed to mixed oxides at 750°C for a few seconds. The powder consists of hollow spheres around 1 μ m, which was calcined at 1000°C for 12h and heated at various temperatures.

Thermal expansion measurements were carried out from room temperature to 1000°C using a Rigaku Thermoflex TAS200TMA with quartz as reference. Cylindrical bars (5 < /> x20mm) were shaped from a calcined body and sintered at 1700°C for x=0 - 0.2, at 1600°C for x=0.3 - 0.6 and at 1500°C for 0.7 - 1.0. The heating and cooling rates were 4K/ min. The density of the samples was measured by Archimedes method.

The electrical conductivity for sintered samples (4xlx40mm) was measured as a function of temperature by the four-probe method. Measurements were performed from room temperature to 1000°C and back with a rate of 1.6°C/min.

The disk with a graded composition was constructed as follows; powder having different composition was laminated in a cylinder (20mm < />, pressed to the disk under 2kb and again pressed hydrostatically under 2kb in a sealed rubber. The sample thus constructed was annealed at 1600°C to accelerate the diffusion and polished finely to observe the interface.

**RESULTS AND DISCUSSION**

The pyrolysis of spray formed by ultrasonic oscillation brings homogeneous hollow spheres around 1 μ m, each of which consist of small primary particles. Figure 1 shows the obtained particles of La₀₉Sr₀ jCrO₃. The 0.5 molar solution of mixed metal ions was oscillated to spray with a rate of 50ml/h and thermally decomposed to the oxides at 750°C. The duration that the spray stays at 750°C was around 5 seconds. As shown in Fig.2, as prepared sample already shows the typical perovskite like patterns although the shape of peaks is broad. The powders thus obtained were calcined at 1000°C, where the primary particles in the sphere coagulate to submicron powders. The sintered disk at 1700°C for 6h shows high density, even for La₀₉sSr₀ jCrO₃ the density was more than 95%.

The XRD patterns for the samples heated at 1400°C are indexed on the basis of the orthorhombic perovskite (Pbnm) except for the rhombohedral perovskite in La₀₉Sr₀ jCr₁-xMnO₃ (x=0 - 0.2). Figure 3 shows the conductivity plots (logo) versus inverse temperature for La₀₉Sr₀ jCr₁-xMnO₃ (sintered at 1400°C) measured from 1000°C to room temperature in air. All samples show semiconductive behavior with a low activation energy and high conductivity. The value of conductivity in this system shows a minimum at around y=0.5. The order of σ = 10² - 10⁵Scm⁻¹ is observed at 1000°C for all composition range.
Figure 4 shows how the thermal expansion coefficient (T.E.C) of La$_{0.9}$Sr$_{0.1}$Cr$_{1-x}$Mn$_x$O$_3$ (measured from 500 to 1000°C) increases with increasing Mn content. The values for La$_{0.8}$Sr$_{0.2}$CrO$_3$ and La$_{0.8}$Sr$_{0.2}$MnO$_3$ are also shown in this figure. The samples were sintered at 1700°C for $x=0$ - 0.2, at 1600°C for $x=0.3$ - 0.6 and at 1500°C for 0.7 - 1.0. The density reaches more than 98% except for $x=0$(La$_{0.9}$Sr$_{0.1}$CrO$_3$, 95%) and La$_{0.8}$Sr$_{0.2}$CrO$_3$, 97%). In our measurements of T.E.C., the difference between (La,Sr)CrO$_3$ and (La,Sr)MnO$_3$ shows
relatively large values of 15%. The absolute value of each sample is slightly different from those reported (2,3). In this study, the values of linear range were taken (500 to 1000°C) for relative evaluation. If the tolerance of thermal expansion compatibility is postulated to be less than a few %, this relatively large difference in T.E.C will have a negative influence on the connection between the electrode and separator and, therefore, lower the cell performance during heat cycling. In addition, the deformation of sintered body will occur during the cofiring process which will be indispensable in the future in order to decrease the fabrication cost of SOFC.

In this study, introduction of a graded structure between La$_{0.9}$Sr$_{0.1}$Cr$_x$O$_3$ (La$_{0.8}$Sr$_{0.2}$CrO$_3$) and La$_{0.9}$Sr$_{0.1}$Mn$_x$O$_3$ (La$_{0.8}$Sr$_{0.2}$MnO$_3$) is tried to relax the stresses induced from the difference in T.E.Cs. Each powder with different composition whose difference in
Fig. 5. SEM photographs and concentration profiles of the cross section at La$_{0.8}$Sr$_{0.2}$MnO$_3$-$\text{La}_{0.8}$Sr$_{0.2}$CrO$_3$. 

La$_{0.8}$Sr$_{0.2}$Mn$_{0.7}$Cr$_{0.3}$O$_3$
Fig. 6. SEM photographs and concentration profiles of the cross section at La$_{0.8}$Sr$_{0.2}$MnO$_3$ - La$_{0.9}$Sr$_{0.1}$Mn$_{0.5}$Cr$_{0.5}$O$_3$ - La$_{0.8}$Sr$_{0.2}$CrO$_3$. 

La$_{0.9}$Sr$_{0.1}$Mn$_{0.5}$Cr$_{0.5}$O$_3$ - La$_{0.8}$Sr$_{0.2}$CrO$_3$ - La$_{0.8}$Sr$_{0.2}$Mn$_{0.3}$O$_3$ - La$_{0.9}$Sr$_{0.1}$Mn$_{0.5}$Cr$_{0.5}$O$_3$ - La$_{0.8}$Sr$_{0.2}$CrO$_3$
Fig. 7. SEM photographs and concentration profiles of the cross section at $La_{0.9}Sr_{0.1}Mn_xCrO_3$ for $x=0, 0.2, 0.4, 0.6, 0.8, 1.0$ boundaries.
T.E.C is in a few % was co-sintered at 1600°C for 48h. Some of the combinations tried are shown below. The powder used were heated at 1400°C in advance to prevent extreme shrinking due to the sintering.

1. La$_{0.8}$Sr$_{0.2}$MnO$_3$ — La$_{0.8}$Sr$_{0.2}$CrO$_3$ (as calcined)
2. La$_{0.8}$Sr$_{0.2}$MnO$_3$ — La$_{0.9}$Sr$_{0.1}$Mn$_{0.5}$Cr$_{0.5}$O$_3$ — La$_{0.8}$Sr$_{0.2}$CrO$_3$
3. La$_{0.8}$Sr$_{0.2}$MnO$_3$ — La$_{0.9}$Sr$_{0.1}$Mn$_{1-x}$Cr$_x$O$_3$ (x=0.2, 0.4, 0.6, 0.8) — La$_{0.8}$Sr$_{0.2}$CrO$_3$

From Fig.5 to 7, the overviews of each graded sintered disk, the near boundary zones of each composition and the concentration profiles by EPMA are shown. Figure 5 is for pure manganite and chromite. When the La$_{0.8}$Sr$_{0.2}$CrO$_3$ powder heated at 1400°C was joined, a good junction was not formed. On the contrary, the as-calcined powder sintered very well and the diffusion of Cr and Mn elements to each side ranged to the extent of 0.1mm. As previously reported, only a slight diffusion occurred when the face to face connected sintered pellets are annealed at high temperature.(5) The powder prepared by the spray pyrolysis method has high reactivity. However, as seen in the cross section photograph of the obtained pellet, a clear bend is observed, which may be due to the difference between sintering rate and thermal expansion rate.

In case 2, La$_{0.9}$Sr$_{0.1}$Mn$_{0.5}$Cr$_{0.5}$O$_3$ having intermediate composition is inserted between La$_{0.8}$Sr$_{0.2}$MnO$_3$ and La$_{0.8}$Sr$_{0.2}$CrO$_3$, where La$_{0.8}$Sr$_{0.2}$CrO$_3$ powder was heated at 1400°C. As shown in Fig.6, wide range of interdiffusion of Cr and Mn elements are observed and the strong connection is realized. The sintered density of La$_{0.8}$Sr$_{0.2}$CrO$_3$ is estimated to be 90% from the measurement of single pellet of La$_{0.8}$Sr$_{0.2}$CrO$_3$. The Case 3 in Fig.7 shows the SEM pictures and profile of pellet connected with six compositions. The difference of the thermal expansion of each composition is in a few %. Wide interdiffusion of each element is also observed, which means a smooth connection is formed at the boundary of each sintered perovskite.

**CONCLUSIONS**

The lanthanum chromite powder obtained from ultrasonic spray pyrolysis method showed high reactivity and good sintering properties. The smooth connection was realized by co-firing each powder sample and the graded structure was well prepared. This shows that the formation of a graded structure on the surface of the separator will relax the stresses from the thermal expansion difference between separator and cathode and, therefore, decrease the voltage drop due to the contact resistance at the boundary of each side.

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