

# Electrochemical properties of a single-cell with a $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ electrolyte strengthened by $\text{Al}_2\text{O}_3$ dispersion.

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We have been carrying out fundamental research on manufacturing and testing cells for reduced-temperature operation using electrolyte-supported cells in which the high oxide-ion conductor of doped  $\text{LaGaO}_3$  is used as an electrolyte. Single-cells with doped  $\text{LaGaO}_3$  electrolytes strengthened by  $\text{Al}_2\text{O}_3$  dispersion were prepared by forming SDC (Samaria-Doped Ceria) interlayers of 0.3  $\mu\text{m}$  thick at 1523 K, before firing the Ni-YSZ cermet anode at 1723 K and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ -SDC composite cathode at 1373 K. The single-cell thus prepared showed the maximum power density of 0.67  $\text{Wcm}^{-2}$  and long-term stability during the operation time of 1000 h at 1073 K.

Key words: Lanthanum gallate, alumina, electrode, solid oxide fuel cell (SOFC)

## 1. INTRODUCTION

Solid oxide fuel cells (SOFCs) are expected as both power generating and co-generating systems with high fuel-to-electricity conversion efficiencies and environmental advantages. Among several types of SOFCs, electrolyte-supported cells using yttria-stabilized zirconia (YSZ) as the electrolyte have many material problems remaining to be solved which are arising from the high operating temperature, typically around 1273 K. A reduction in the operating temperature leads to the benefits which include use of low-cost metallic separators instead of more expensive ceramic ones, better long-term performance stability, and system compactness by reducing the thickness of the heat insulator. Therefore, we have been carrying out fundamental research on manufacturing and testing the cells for reduced-temperature operation using electrolyte-supported cells in which doped  $\text{LaGaO}_3$  is used as the electrolyte as well as using electrode-supported cells with a thin YSZ electrolyte film on thick porous anodes. The doped  $\text{LaGaO}_3$  has been known as a high oxide-ion conductor [1]. The  $\text{LaGaO}_3$ -based materials, however, are mechanically weak in spite of its quite good sinterability [2]. In a previous study [3], we have found that 2 wt%  $\text{Al}_2\text{O}_3$  dispersion into the doped  $\text{LaGaO}_3$  electrolyte can improve the mechanical properties without altering the thermal expansion coefficient and ionic conductivity. In this study, we have prepared electrochemical cells with the doped  $\text{LaGaO}_3$  electrolyte strengthened by  $\text{Al}_2\text{O}_3$  dispersion to investigate their electrochemical property and long-term stability.

## 2. EXPERIMENTAL

### 2.1 Anode preparation

A cermet electrode made of Ni, Ce-doped

YSZ and Sm-doped  $\text{CeO}_2$  was used as an anode. Zirconium octylate ( $\text{Zr}(\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2)_4$ , Nihon-Kagaku-Sangyo), cerium octylate ( $\text{Ce}(\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2)_4$ , Nihon-Kagaku-Sangyo) and yttrium octylate ( $\text{Y}(\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2)_3$ , Nihon-Kagaku-Sangyo) were used as metallo-organic precursors of Ce-doped YSZ, and NiO powder as a starting material of Ni. Zr-, Ce- and Y-octylates were dissolved in toluene (purity: 99.5%). The solution of metallo-organic precursors was prepared by mixing the three octylate solutions at the ratio corresponding to the composition of  $(\text{CeO}_2)_{0.1}[(\text{Y}_2\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.92}]_{0.9}$  (this particular composition will hereafter be abbreviated as CeYSZ). The NiO powder and  $\text{Sm}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$  (this particular composition will hereafter be abbreviated as SDC10) powder were then mixed with the solution to prepare a slurry. Sm content of 0.1 in the solid-solution of SDC10 was chosen for its higher electronic conductivity than that of  $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (this particular composition will hereafter be abbreviated as SDC20) [4]. The slurry was adjusted so that the content of the CeYSZ in the Ni-CeYSZ-SDC10 cermet is 10 wt%. The NiO-CeYSZ-SDC10 composite was obtained through hydrolysis, polymerization by condensation and thermal decomposition of the metallo-organic precursors in the slurry. The temperature of the hydrolysis, condensation, thermal decomposition and sintering were 303, 303, 773, 1723 K, respectively. The analysis of the metallo-organic precursors was carried out by a gel permeation chromatography (GPC) (TSK HLC-8120GPC, Toso, Japan). For the thermal analysis of the precursors, differential thermal analysis (DTA) (DTA-50, Shimadzu, Japan) was conducted at a heating rate of 1  $^\circ\text{C}/\text{min}$  in a flow of air.

## 2.2 Cathode preparation

The powders of La<sub>0.7</sub>Sr<sub>0.3</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub> (this particular composition will hereafter be abbreviated as LSCF) and SDC20 prepared by combustion synthesis technique (Praxair Specialty Ceramics, USA) were used as the raw material. The SDC20 powder was mixed with the LSCF powder, screen printed onto the electrolyte, and then sintered at 1373 K for 4 h.

## 2.3 Electrochemical cells

Dense sheets of 0.2 mm thick made of La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>2.85</sub> (this particular composition will hereafter be abbreviated as LSGM) with Al<sub>2</sub>O<sub>3</sub> dispersion were used as the electrolyte. The preparation method of the LSGM-Al<sub>2</sub>O<sub>3</sub> electrolyte has been described in Ref. [3]. Single-cells with doped LaGaO<sub>3</sub> electrolytes strengthened by Al<sub>2</sub>O<sub>3</sub> dispersion were prepared by forming SDC20 interlayers of 0.3 μm thick at 1523 K, before firing the Ni-CeYSZ-SDC10 cermet anode and LSCF-SDC20 composite cathode. The single-cell thus prepared had a nominal size of 60x60 mm<sup>2</sup> with an effective electrode area of 4 cm<sup>2</sup>. The microstructure of the SDC20 layer was observed using a scanning electron microscope (SEM) (JSM-5400, JEOL, Japan). The V-I characteristics of the cell was measured at 923-1073 K using a current-pulse generator (Hokuto Denko HC-110) with H<sub>2</sub> as a fuel and air as an oxidizer. The preparation method of half-cells and experimental techniques used for measuring electrochemical properties of the electrodes have been described in detail in a previous paper [5].

## 3. RESULTS AND DISCUSSION

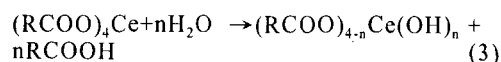
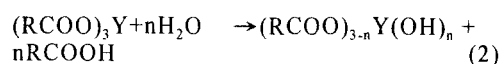
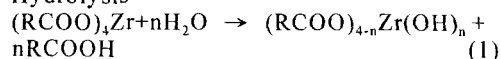
## 3.1 Ni-CeYSZ-SDC10 cermet anode

## 3.1.1 Characterization of the metallo-organic precursors

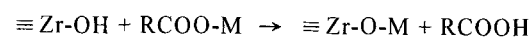
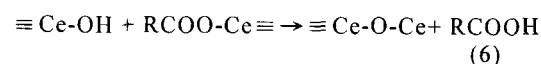
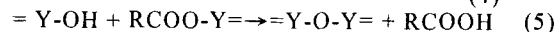
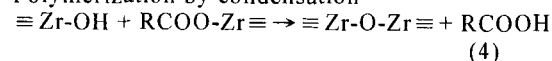
## (a) Hydrolysis and polymerization

The solution of metallo-organic precursors for CeYSZ easily reacts with moisture in the atmosphere causing gelation. The gelation of precursors, similar to the metal alkoxides, can be represented by hydrolysis and polymerization by condensation as shown in reactions (1) - (7),

## Hydrolysis



## Polymerization by condensation



(7)

where R is C<sub>7</sub>H<sub>15</sub>, and M is Y or Ce.

The GPC analysis was conducted for the precursors which were exposed to 3 % humidified air for 100 h at room temperature, and the results are listed in Table 1. Three groups of molecules were found to exist. From estimation of molecular weights, peak 3 should be assigned to RCOOH (R=C<sub>7</sub>H<sub>15</sub>). The content of RCOOH was found to be relatively high as 36%, which is accounted for by RCOOH produced in the reactions (1)-(7). Peak 2 is assigned to (RCOO)Zr(OH)<sub>3</sub>, (RCOO)Y(OH)<sub>2</sub>, and (RCOO)Ce(OH)<sub>3</sub> which are considered to be formed by the hydrolysis. They correspond to n = 3 and n = 2 in the reactions (1), (2) and (3), respectively, and amount to 48% of the total content. Peak 1 is assigned to oligomers formed by the polymerization. From the molecular weights we have concluded that the oligomers generated by the gelation were mainly made up of 3 or 4 monomers.

Table 1. Results of GPC analysis.

	Peak 1	Peak 2	Peak 3
Peak Top (min.)	9.91	10.39	10.87
Mean molecular weight			
by number (Mn)	1019	245	140
by weight (Mw)	1057	263	145
by viscosity (Mv)	1057	263	145
Area (mVsec)	3.23	10.4	7.83

## (b) Thermal decomposition

Yttrium and cerium atoms in the compounds, ≡Zr-O-Y≡ and ≡Zr-O-Ce≡, formed by the reactions (7) already have bonds with zirconium atoms through O atoms and will be easily doped into ZrO<sub>2</sub> through thermal decomposition to form a solid-solution of CeYSZ. Unreacted zirconium-, yttrium- and cerium-octylates which may exist in the slurry even after gelation should decompose into ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>, respectively, similarly to the thermal decomposition of metal fatty acid salts [6]. The DTA curves of Zr-, Y- and Ce-octylates were measured in air with a heating rate of 1 °C/min. Each curve showed a strong exothermic peak which can be attributed to the decomposition of Zr-, Y- and Ce-octylates into oxides [7]. The decomposition temperatures of the octylates were found to be close to one another. ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> formed from the mixed solution of Zr-, Y- and Ce-octylates, therefore, were finely mixed to form a uniform solid-solution of CeYSZ. Thus, the NiO-CeYSZ-SDC10 composite will be obtained through hydrolysis, condensation and thermal decomposition of the octylates in the slurry which consists of the NiO powder, SDC10 powder and the octylates.

### 3.1.2 Steady-state polarization and durability

Since the CeYSZ particles thus prepared are fine [8,9], the number of active sites at the anode/electrolyte interface is expected to be large enough for reduced-temperature operation, and Ni particles hardly agglomerate. The steady-state polarization of the anode on the SDC20 interlayer was measured at 1073 K using a half cell with YSZ electrolyte on which the SDC20 layer was formed. The result is shown in Fig. 1. Overpotential of the anode was found to be 27.5 mV at a current density of  $0.3 \text{ Acm}^{-2}$ . It has been confirmed by continuous operation for 2000 h that the anode performance is very stable and degradation is negligible.

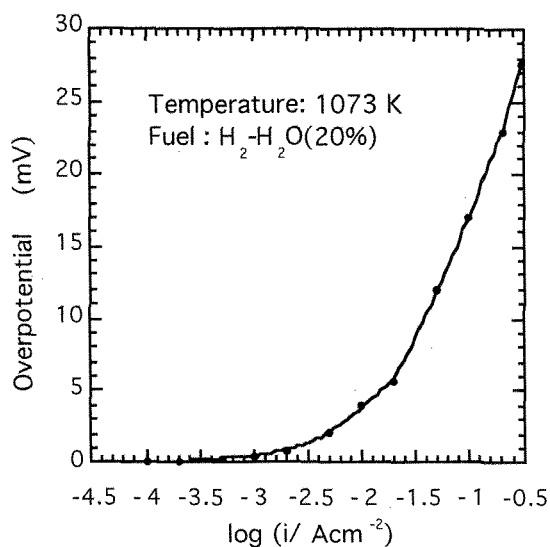


Fig. 1. Steady-state polarization of the Ni-CeYSZ-SDC10 cermet anode on YSZ electrolyte with SDC20 interlayer.

### 3.2 LSCF-SDC20 composite cathode

In order to obtain high electrode activity, it is critically important to control the composition and microstructure. As for the cathode, a relationship between overpotential and SDC content in the LSCF-SDC composite at 1073 K has been investigated using an electrolyte made of SDC20. The overpotential was found to be dependent on the SDC20 content to give a minimum of 64 mV at a current density of  $0.3 \text{ Acm}^{-2}$  at a specific SDC content of around 30 wt%. Figure 2 shows the result of durability test of the cathode with SDC20 content of 30 wt% on the electrolyte made of SDC20 at 1073 K. The cathode exhibited excellent durability for 900 h. During the test, the cathode was cooled down to room temperature once, and then heated to the operation temperature of 1073 K again. The degradation of the cathode performance was not observed even after this thermal cycle. Furthermore, we have already reported that the LSCF-SDC/SDC bi-layer cathode has high resistance against degradation by chromium-poisoning [10,11].

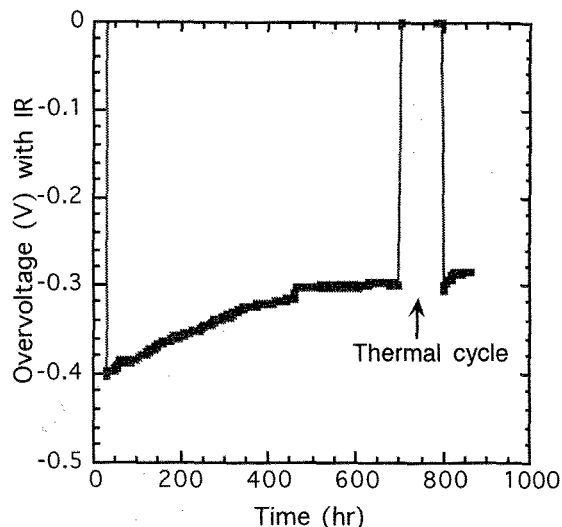


Fig. 2. Durability of the LSCF-SDC composite cathode on an SDC20 electrolyte.

### 3.3 Single-cell with the doped LaGaO<sub>3</sub> electrolyte strengthened by Al<sub>2</sub>O<sub>3</sub> dispersion

SDC interlayers of approximately  $0.3 \mu\text{m}$  thick were fired onto both surface of the electrolyte at 1523 K to prevent reactions and excessive interdiffusion between the electrodes and the electrolyte. Figure 3 shows the SEM micrograph of the electrolyte surface (a) before and (b) after the deposition of SDC20 layers. The micrograph clearly shows that the SDC20 layer deposited densely and finely on the LSGM electrolyte. The apparent grain size of the SDC20 was found to be as small as  $0.5 \mu\text{m}$ . After the preparation of the SDC20 interlayer, the anode and the cathode were fired at 1723 and 1373 K, respectively.

Figure 4 shows the V-I characteristics of the single-cell measured in the temperature range from 923 to 1073 K using H<sub>2</sub> as the fuel and air as the oxidizer. Maximum power densities of 0.67, 0.58, 0.46 and  $0.29 \text{ Wcm}^{-2}$  were obtained at 1073, 1023, 973 and 923 K respectively, which indicates that the single-cell has good performance even at reduced temperatures below 1073 K. Detailed electrochemical analyses indicated that the voltage losses at 1073 K due to an ohmic resistance, a cathode overpotential, and an anode overpotential were 51, 64 and 28 mV, respectively at a current density of  $0.3 \text{ Acm}^{-2}$ .

Figure 5 shows the results of a durability test of the single-cell at a current density of  $0.3 \text{ Acm}^{-2}$ . It is to be noted that the cell did not degraded during the 1000 h test at 1073 K. Thus the single-cell made of the doped LaGaO<sub>3</sub> electrolyte strengthened by Al<sub>2</sub>O<sub>3</sub> dispersion and the improved electrodes has been proved to give excellent electrochemical performance for a long time.

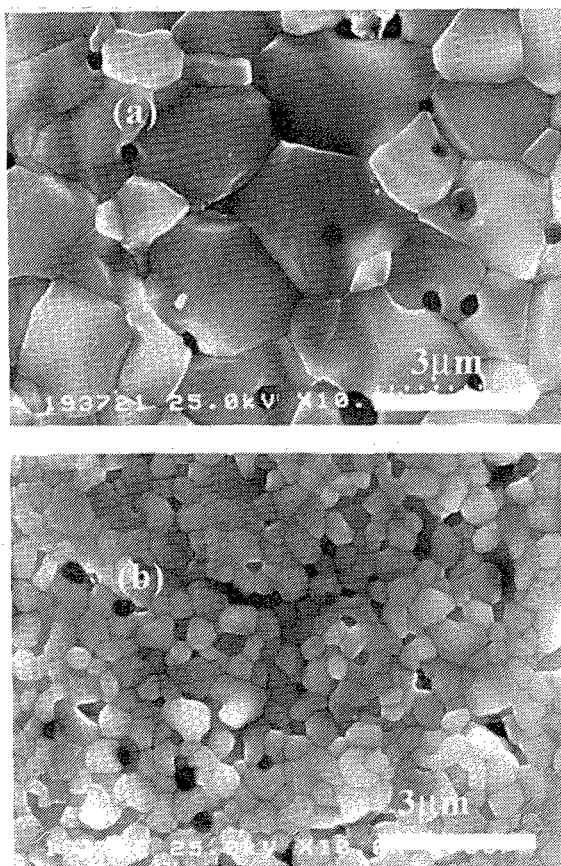


Fig. 3. SEM images of the surface of the electrolyte. (a) before and (b) after SDC coating.

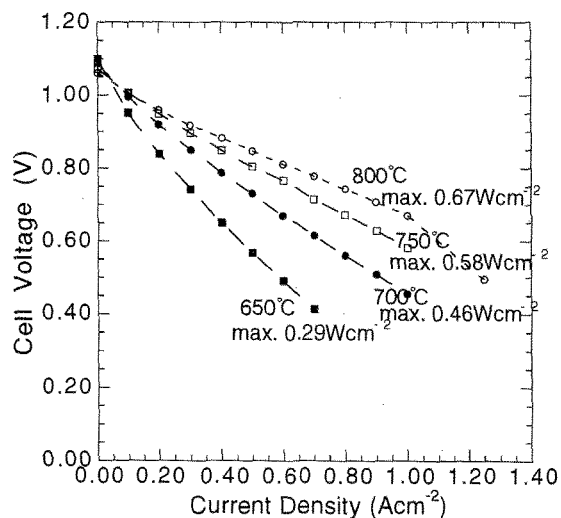


Fig. 4. V-I characteristics of the single-cell.

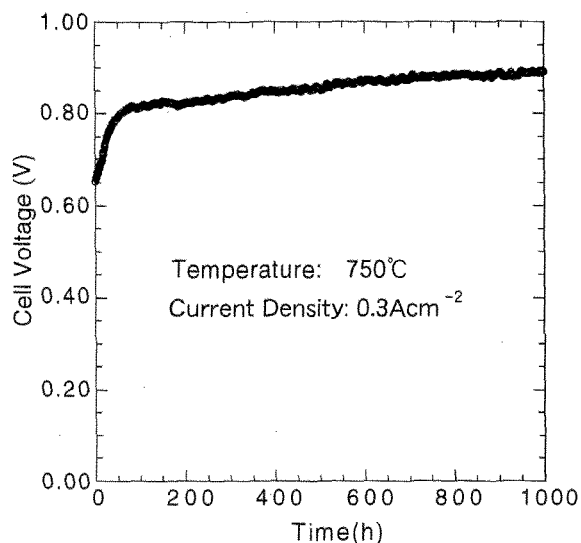


Fig. 5. Durability of the single-cell at a current density of  $0.3 \text{ Acm}^{-2}$ .

#### 4. Conclusion

Electrolyte-supported cells in which the high oxide-ion conductor of doped  $\text{LaGaO}_3$  strengthened by  $\text{Al}_2\text{O}_3$  dispersion is used as the electrolyte have been manufactured and tested as reduced-temperature solid oxide fuel cells. Single-cells with the electrolyte were prepared by forming SDC interlayers of  $0.3 \mu\text{m}$  thick at  $1523 \text{ K}$ , before firing the Ni-YSZ-SDC10 cermet anode at  $1723 \text{ K}$  and LSCF-SDC20 composite cathode at  $1373 \text{ K}$ . The single-cell thus prepared showed the maximum power density up to  $0.67 \text{ Wcm}^{-2}$  and long-term stability during the operation time of  $1000 \text{ h}$  at  $1073 \text{ K}$ .

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