ABSTRACT

$Y_{1-x}Sr_xCo_{0.7}Fe_{0.3}O_3$ ($X=0.2-0.8$) was investigated as a cathode material for SOFC. The overpotential at 800°C was below 20mV at 400mA/cm$^2$, which represents a high cathodic activity compared to other cathode materials. The thermal expansion coefficients (TECs) were in the range of approximately $10^{-6}$ to $20\times10^6$ K$^{-1}$, which strongly depended on the system composition.

INTRODUCTION

Solid oxide fuel cells (SOFC) are expected to be a new power generation system because of their high efficiency. However, several improvements must be made for commercial use. One of the important issues is to lower the operating temperature below 800°C, since high temperature limits the selection of the construction materials. Reducing the operating temperature causes an increase in the overpotential of SOFC cathode. Therefore, it is important to develop a cathode with lower overpotential at lower temperatures.

The properties required of a cathode material are (i) high electric and ionic conductivity, (ii) high catalytic activity for oxygen reduction, (iii) chemical and thermal compatibility with the electrolyte, and (iv) chemical stability in an oxidizing atmosphere. Of these properties, (i) and (ii) are related to electrode performance, and (iii) and (iv) are related to long-term stability and durability at the operation temperature.

$La_{1-x}Sr_xMnO_3$ (LSM) has been commonly used as the cathode material for SOFCs, because of its high catalytic activity for oxygen reduction at high temperatures and its thermal and chemical compatibility with yttria stabilized zirconia (YSZ) (1,2). YSZ is used as the electrolyte for its high ionic conductivity at 1000°C. Recently, rare earth-doped cobaltite has attracted much attention as SOFC cathode for its high activity at lower temperatures. It is reported that doping Sm or Gd to cobaltite increases its cathodic activity (3). However, its chemical compatibility with YSZ is poor, and TEC is high and incompatible with the electrolyte material. Electrolytes such as Sm doped ceria show high ionic conductivity at lower temperatures and they are also chemically stable with cobaltite. Yamamoto et al. has studied many Gd doped Co based perovskite cathodes and...
showed that doping Mn in the B-site can lower the thermal expansion (4, 5, 6). Lee et al. reported that $Y_{0.8}Ca_{0.2}Co_{0.3}Fe_{0.7}O_3$ (YCCF8273) shows superior oxygen reduction compared to LSM, and its TEC was close to that of YSZ (7). Several studies have indicated that LSCF showed compatible TEC with the electrolyte, but the cathodic activity was not as high as $La_{1-x}Sr_xCoO_3$ (LSC). Furthermore, the known resources of raw materials such as Gd, Sm are limited and are not sufficient for commercial use on a large scale.

In this paper, we synthesized $Y_{1-x}Sr_xCo_{0.7}Fe_{0.3}O_3$ (YSCF) ($X=0.2-0.8$) as cathode materials, and their cathodic overpotential, thermal expansion coefficients and reactivity with electrolytes were investigated.

**EXPERIMENTAL**

**Preparation of Material**

YSCF was prepared using a sol-gel method. All raw materials were chemical grades (Wako Chemical, Kanto Chemical) and their impurity levels were less than 0.1%. Aqueous solutions of $Y(NO_3)_3$, $Sr(NO_3)_2$, $Co(NO_3)_2$, $Fe(NO_3)_3$ were mixed in a given stoichiometric ratio, then an excess molar of citric acid was added to the solution. Equimolar ethylene glycol was then added to the solution. The solution was heated at 120°C on a hot plate. Resultant polymer was pyrolyzed in air at 400°C. Then the product was calcined in air at 1000°C.

The ratio of each ion in the product was measured by a ICP (Shimadzu), crystal forms of powders were characterized by a X-ray diffraction analysis (XRD) (Rigaku), and particle size was measured by a scanning electron microscopy (SEM).

**Measurements**

Synthesized powder was uniaxially pressed into a pellet at 20MPa, and sintered at 1300°C for 2 hours. TEC of the pellet from room temperature to 1000°C at a rate of 4°C/min was measured (Shimadzu, TMA-50) using quartz as a reference.

Sintered samarium doped ceria (SDC) disks (20 mol % Sm doped, supplied by Token Sangyo Co., Ltd.) were used for the electrolyte. Its dimension was 10mm in diameter and 0.5mm in thickness. The synthesized electrode powder was mixed with binder prepared from $\alpha$-terpineol and ethyl-cellulose, and was coated on the YSZ disk by tape-casting method. The coated disk was fired at 1100°C for 4 hours. Platinum paste was painted on the other side of the disk for counter and reference electrodes.

Steady-state cathodic polarization was measured by eliminating IR-drop with a current interruption method at 800°C in air. AC impedance spectroscopy was measured by using a potentiostat (Tohogiken, Inc.) and a frequency response analyzer (NF Corp.) connected to a personal computer.

The electrical conductivity of the sintered sample was measured in air by a 4-probe technique. The dimension of the sintered sample was 0.08x1x0.5 cm.
The reactivity of the sample with YSZ was investigated. The powders of YSCF and YSZ were mixed in 10:1 molar ratio, and then the mixture was annealed at 1000°C for 10 hours. The annealed powders were assessed with XRD to qualify the reactivity.

RESULTS AND DISCUSSION

X-ray Diffraction Analysis

The observed phase and lattice parameters of YSCF at ambient temperature are summarized in Table I. The structure of all the samples was distorted perovskite structure, i.e. orthorhombic with the space group Pbnm. Cell volume decreased as the content of Y increased. The XRD index and the lattice parameter of \( \text{Y}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3} \) (YSCF8273) were similar to that of YCCF8273 reported by Lee et al. (7)

| Sample     | X     | structure   | a(Å) | b(Å)  | c(Å)  | cell volume |
|------------|-------|-------------|------|-------|-------|-------------|
| YSCF2873   | 0.2   | orthorhombic| 5.43 | 5.43  | 7.69  | 226.9       |
| YSCF4673   | 0.4   | orthorhombic| 5.32 | 5.47  | 7.61  | 221.6       |
| YSCF5573   | 0.5   | orthorhombic| 5.29 | 5.42  | 7.65  | 219.2       |
| YSCF6473   | 0.6   | orthorhombic| 5.30 | 5.42  | 7.65  | 219.4       |
| YSCF7373   | 0.7   | orthorhombic| 5.29 | 5.41  | 7.64  | 218.8       |
| YSCF8273   | 0.8   | orthorhombic| 5.20 | 5.47  | 7.47  | 212.5       |

Reactivity with YSZ

To investigate the reactivity, YSCF powders were mixed with YSZ or SDC powders and annealed for 10 hours at 1000°C. YSCF powders reacted with YSZ powders to form \( \text{SrZrO}_3 \) as shown in Fig. 1. On the other hand, the powders did not react with SDC powders. Thus, SDC disk was used as the electrolyte for electrochemical measurements.

Electrochemical Measurements

Cathodic activities of YSCF electrodes on SDC electrolyte were measured. Figure 2 shows the cathodic overpotential vs. current density of YSCF at 800°C as a function of doping ratio. Overpotentials of LSC and LSCF are also plotted for comparison. YSCF4673 showed the lowest overpotential among them, i.e. below 20mV at 400mA/cm\(^2\). This overpotential is higher than for LSC but lower than for LSCF, which is sufficiently low for SOFC cathode.

Figure 3 shows the temperature dependence of the cathodic overpotential of YSCF. The overpotential decreases as the temperature increases, indicating improved cathodic activity. The YSCF electrodes show promising performance as cathodes for solid oxide fuel cells.
YSCF4673. The overpotential is below 5mV at 850°C and below 40mV for 750°C. This indicates that this material can be used even at lower temperatures. Figure 4 shows the impedance spectra of YSCF4673 at 750-850°C. It can be seen that the resistance at the intercept of the semi-circle, representing cathodic reaction, decreases as the temperature increases. Interfacial conductivity (σ_e) was calculated from the resistance at the intercept as,

$$\sigma_e = 1/(R \cdot A)$$

where R is electrode resistance and A is the area of the electrode. Figure 5 shows the temperature dependence of σ_e. Activation energy was calculated to be 200kJ/mol.

The chemical composition is not the only factor that affects the overpotential. As we have reported elsewhere (8), both physical properties and structure influence the cathodic reaction rate. There are two types of cathodic reaction mechanism, one for cathode with high ionic conductivity, e.g. for LSC, and the other for cathode with low ionic conductivity, e.g. for LSM. If the material has high ionic conductivity, the surface area determines the reaction rate. On the other hand, for the material with low ionic conductivity, the three phase boundary contributes to the reaction rate.

The ionic conductivity of YCCF8273, measured by Lee, was 2.0 x 10^{-5} S/cm at 750°C, 0.209 bar (7). Although it is not as low as that of LSM, it is more than 4 orders of magnitude lower than that of LSC. The ionic conductivity of YSCF8273 is considered to be not so different from YCCF8273. Thus it is assumed that the reaction mechanism of YSCF8273 is similar to that of LSM than to that of LSC. The SEM image of the electrode in Fig. 6 shows that the particle size of the YSCF electrode is approximately 0.5-1µm. From our previous study (9) three phase boundary length was estimated to be 50µm/µm². The three phase boundary length of this electrode could not be accurately measured because the imprints of the particles were not clearly observed. From this estimated value, the overpotential should be smaller if the rate constants of YSCF8273 were similar to that of LSM (10). The three phase boundary length of YSCF4673 was similar to that of YSCF8273. Since the overpotential of YSCF4673 is smaller than that of YSCF8273, it is indicated that ionic conductivity of YSCF4673 is higher. Thus the reaction mechanism seems to be similar to that of LSC. However, further investigation on ionic conductivity, the rate of adsorption and desorption and surface area of YSCF is needed to clarify the reaction mechanism.

**Electrical Conductivity**

Electrical conductivity of the sintered sample of YSCF(0.2-0.8) was measured. Figure 7 shows the diagrams of log (σT) vs. T, where σ is the electrical conductivity and T is the absolute temperature. The electrical conductivity behavior of YSCF was similar to that of LSM

**Thermal Expansion**

TEC of the electrode must match with that of the electrolyte for practical use. Figure 8 shows the thermal expansion rate as a function of doping ratio, X. TEC was approximately 20x10^{-6} K^{-1} for YSCF4673, which is much higher than that of YSZ and
SDC. For YSCF5573, however, TEC was as low as 10×10^6 K^−1. In this system, the effect of composition on TEC is large, which provides an effective method to control TEC by adjusting composition.

**CONCLUSIONS**

\[ Y_{1-x}Sr_xCo_{0.7}Fe_{0.3}O_3 \ (X=0.2–0.8) \] was investigated as a cathode material for SOFC. The overpotential at 800°C was below 20mV at 400mA/cm^2, which represents a high cathodic activity compared to other materials. TECs were in the range of 10–20×10^6 K^−1.

**REFERENCES**

1. O. Yamamoto, Y. Takeda, R. Kanno, H.U. Anderson, *Solid State Ionics*, 22, 241 (1987)
2. A. Hammouche, E. Siebert and A. Hammou, *Mat. Res. Bull.*, 24, 367 (1989)
3. T. Ishihara, M. Honda, T. Shibayama, H. Minami, H. Nishiguchi, Y. Takita, *J. Electrochem. Soc.*, 145, 3177 (1998)
4. H.Y. Tu, M.B. Phillipps, Y. Takeda, T. Ichikawa, N. Imanishi, N.M. Sammes and O. Yamamoto, *J. Electrochem. Soc.*, 146, 2085 (1999)
5. M. Phillipps, N. Sammes, Y. Takeda and O. Yamamoto, *Denki Kagaku*, 64, 544 (1996)
6. O. Yamamoto, S. Watanabe, H. Ueno, N. Imanishi, Y. Takeda, N. Sammes, M.B. Phillipps, in Solid Oxide Fuel Cells IV, M. Dokiya, O. Yamamoto, H. Tagawa and S.C. Singhal, Editors, PV95-1, p.414, The Electrochemical Society Proceedings Series, Pennington, NJ (1995)
7. H.Y. Lee, S.M. Oh, I.-Y. Seo, F. Rocholl and H.-D. Wiemhöfer, in *Solid Oxide Fuel Cells V*, U. Stimming, S.C. Singhal, H. Tagawa and W. Lehnert, Editors, PV97-40, p.520, The Electrochemical Society Proceedings Series, Pennington, NJ (1997)
8. H. Fukunaga, T. Akatsuka, A. Endo, C. Wen and K. Yamada, in *Solid Oxide Fuel Cells VI*, S.C. Singhal and M. Dokiya, Editors, PV99-19, p.443, The Electrochemical Society Proceedings Series, Pennington, NJ (1999)
9. H. Fukunaga, C. Wen and K. Yamada, *J. Ceramic Soc of Japan*, 107, 229 (1999)
10. H. Fukunaga, M. Ihara, K. Sakaki and K. Yamada, *Solid State Ionics*, 86-88, 1179 (1996)
Fig. 1 XRD patterns of the mixture of YSCF4628 and YSZ after annealing at 100°C for 10 hours ○YSZ, ●SrZrO$_3$.

Fig. 2 Cathodic overpotential vs. current density of YSCF at 800°C
Fig. 3 Temperature dependence of the cathodic overpotential of YSCF 4673.

Fig. 4 AC impedance spectra of YSCF4673 in air
Fig. 5 The temperature dependence of interfacial conductivity of the cathode.

Fig. 6 SEM image of the surface of YSCF8273 electrode.
Fig. 7 Electrical conductivity of the sintered sample of YSCF vs. temperature

Fig. 8 Thermal expansion behavior of YSCF