APPLICATION OF (Sm$_{0.5}$Sr$_{0.5}$)Co$_3$ TO (Zr, Sc)O$_2$ ELECTROLYTE SOFCs FOR REDUCED TEMPERATURE OPERATION

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ABSTRACT

Application of (Sm$_{0.5}$Sr$_{0.5}$)Co$_3$ (SSC) as a cathode material on Zr$_{0.85}$Sc$_{0.15}$Co$_{0.01}$O$_{1.95}$ electrolyte for reduced temperature operation SOFCs was investigated in detail. As a protective layer for the electrolyte, doped ceria thin films were fabricated on the electrolyte by a cost effective wet ceramic process using nanometer Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ and submicrometer Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ powders. The impact of doped ceria interlayer on the performance of (Sm$_{0.5}$Sr$_{0.5}$)Co$_3$ cathode was investigated by XRD and AC impedance measurements. It was found that controlling the microstructure of the interlayer is important for (Sm$_{0.5}$Sr$_{0.5}$)Co$_3$ cathodic performance. The SSC cathode deposited on SSZ electrolyte coated by (Ce$_{0.8}$Sm$_{0.2}$)O$_{1.9}$ or (Ce$_{0.9}$Gd$_{0.1}$)O$_{1.95}$ interlayer can reach an interface conductivity of 4.4 S/cm$^2$ or 7.2 S/cm$^2$ at 700°C, respectively.

INTRODUCTION

Lowering the operating temperature of solid oxide fuel cells (SOFCs) can accelerate the commercialization of this energy conversion technology. By reducing the operating temperature to around/or less than 700°C, lower cost and long-term durability of SOFCs can be achieved since (i) some relatively inexpensive metallic materials can be employed, (ii) degradation of materials can be retarded, and (iii) much more flexible stack designs can be adopted. In order to lower the operating temperature, along with the problem of suppressing the increase in ohmic resistance, which can be solved by employing alternative electrolyte materials with higher ionic conductivity and/or reducing the thickness of the electrolyte, minimizing polarization resistances occurring at electrode/electrolyte interfaces, is important. The interfacial resistances, especially the resistance of oxygen reduction reaction, are dramatically increased as the operating temperature is reduced. Therefore, selecting a high-performance cathode material and constructing a suitable cathode/electrolyte interface are major challenges facing the development of reduced temperature SOFCs.

Strontium-doped rare earth cobaltite oxides, (Ln$_{1-x}$Sr$_x$)Co$_3$ (Ln=La, Pr, Sm, Gd, etc.), especially (Sm$_{0.5}$Sr$_{0.5}$)Co$_3$, have been widely considered as cathode materials for reduced temperature SOFCs with doped-ceria or LSGM electrolyte because the cobaltites
possess excellent mixed-conduction characteristics, relatively high ionic conductivity, high catalytic activity for oxygen reduction and good chemical compatibility with the electrolytes (1-4). However, because both mentioned electrolytes have disadvantages such as electronic conductivity, high cost, and difficulties in processing, usage of traditional stabilized zirconia electrolytes is desired despite of stabilized zirconia electrolytes exhibiting detrimental reaction with strontium-doped cobaltites. One approach to resolving this drawback is to deposit a doped ceria thin film as a protective layer on stabilized zirconia electrolyte (5). In our previous studies, a few μm thick GDC interlayer was prepared by a cost effective wet ceramic process, and it suppressed successfully the solid-state reaction between zirconia electrolyte and (La0.6Sr0.4)CoO3 (6, 7). An anode supported tubular SOFC with such structure generated electricity successfully at around 700°C (8); performance at even lower temperatures can be enhanced by further optimizing the cathode and the interlayer.

In this paper, we present some results of the recent efforts towards improving the performance of SOFCs at reduced temperatures. The work focused on the improvement of functional layers. A scandia-stabilized zirconia electrolyte was utilized because this material has twice to triple the ionic conductivity of traditional YSZ. (La0.6Sr0.4)CoO3 was replaced by (Sm0.5Sr0.5)CoO3 because the latter shows a better cathodic performance. Doped ceria interlayers were prepared using nanometer Ce0.8Sm0.2O1.9 and submicrometer Ce0.9Gd0.1O1.95 powders. We expected that by using the nanopowder, a thinner interlayer with better adhesion to zirconia electrolyte can be achieved at a reduced firing temperature; this is desired for suppressing the contact resistance as well as the unfavorable reaction between doped ceria interlayer and stabilized zirconia electrolyte. Furthermore, a relatively lower cathodic polarization resistance is also expected for SDC/SSC interface, compared to that of the GDC/SSC case. Primary results confirmed the validity of the SDC and GDC interlayers for preventing the unfavorable solid-state reactions between SSC cathode and SSZ electrolyte. The interface conductivity of 4.4 S/cm², and 7.2 S/cm² at 700°C, with the activation energy of ca. 1.3 eV, was achieved for SSC cathode prepared on SDC and GDC interlayer, respectively.

EXPERIMENTAL

For the electrolyte material, ceria-doped scandia-stabilized zirconia, Zr0.85Sc0.1Ce0.01O1.95 (SSZ, Daiiti Kigenso Kagaku Kogyo) powder was used. Doped ceria interlayers were prepared using commercially available nanometer Ce0.8Sm0.2O1.9 (SDC, MicroCoating Technologies) and submicrometer Ce0.9Gd0.1O1.95 (GDC, Anan Kasei) powders. (Sm0.5Sr0.5)CoO3 (SSC) cathode powder was prepared by the coprecipitation method (9). After heating in air at 900°C for 5 h, the obtained powder was mostly converted to the desired perovskite structure, as determined by X-ray diffraction.

SSZ powder was pressed and then sintered at 1320°C for 3 h into uniform pellets of 21.5 mm in diameter and 2.25 mm in thickness with a relative density of more than 96%. Slurry dip-coating technique was adopted for preparing doped ceria interlayer on SSZ disks. Slurries were prepared by ball milling the doped ceria powders in a solvent comprised of isopropanol and toluene together with some others organic additives such as...
PVB (binder), fish oil (dispersant), di-n-butyl-phtalate (plasticizer), and Triton-X (bubble-killing reagent). GDC interlayers were prepared by coating once both faces of SSZ disks with the slurry, and then firing the samples at 1200°C for 2 h in air. For the case of SDC, single and double coated interlayers were prepared. The preparation of single coated SDC interlayers was similar to that of GDC interlayer. The double coated SDC interlayer was also prepared by a similar process, but the first coated SDC green layer was calcined at 900°C for 1 h in air before the subsequent coating of the SDC slurry on it. The SSZ disks coated by an interlayer are designated as SSZ/GDC, SSZ/SDC-1, and SSZ/SDC-2, respectively. The microstructure of the samples was observed by scanning electron microscopy (SEM, JMS-6310F, Jeol).

The impact of doped ceria interlayers in preventing the unfavorable solid-state reactions between SSC cathode and SSZ electrolyte was examined by X-ray diffraction measurements. A layer with few μm thickness of SSC was deposited by painting a paste, which was prepared from SSC powder, cellulose acetate, and turpentine oil, on the doped ceria interlayers, and then firing the samples at 900, 1000 and 1100°C for 1 h in air. X-ray diffraction analysis was performed using monochromated CuKα radiation at 40 kV and 50 mA (Rint-Ultima, Rigaku Corp.). Since SSC and doped ceria interlayers were thin enough, the interfacial reactions could be studied by XRD analysis of the surface of samples.

In order to estimate the performance of SSC on SSZ/doped ceria interlayer samples, interfacial conductivity and cathodic overpotential were measured by a three-terminal method. A symmetrical half-cell configuration was adopted. Circular SSC electrodes were prepared by painting the SSC paste on the center of both faces of each doped-ceria/SSZ/doped-ceria sample, and then firing at 950°C for 1 h in air. The SSC electrodes were ca. 30 μm thick and 0.37 cm² surface area. As a reference electrode, Pt paste (Tanaka Kikinzoku Kogyo K. K) was painted at the side of the SSZ disks and fired at 900°C for 30 min. AC complex impedance measurements were performed between 600 and 800°C in air using a frequency analyzer (Solartron 1260) and a potentiostat (Solartron 1286) over the frequency range of 1 MHz to 10 mHz. The amplitude of the AC signal imposed on the samples was 10 mV. Cathodic overpotential was also measured with the frequency analyzer. Performances of SSC electrodes deposited directly on SSZ and GDC disks were used as reference for estimating the effects of the interlayers.

**RESULTS AND DISCUSSION**

Fig. 1 depicts SEM features of doped ceria interlayers deposited on dense SSZ disks. Fracture views (Fig. 1a, c, and e) show that the interlayers were thin and uniform. Thicknesses of the interlayers were about 1 and 2 μm, depending on the preparation conditions. The single coated SDC interlayer was ca. 1 μm in thickness (Fig. 1a), while double coated SDC (Fig. 1c) and GDC (Fig. 1e) interlayers were ca. 2 μm thick. All interlayers adhered firmly to the substrates. Because the interlayers were deposited on sintered substrates, only doped ceria particles shrank. Therefore, ultra-fine openings exist inside the interlayers. Figs. 1b, d, and f show a top view of the interlayers.
Figure 1. SEM images of cross-section and surface for various doped ceria films deposited on a SSZ disk: (a), (b) single coated SDC; (c), (d), (g) double coated SDC; (e), (f), (h) GDC.

Submicrometer GDC powder yielded the most homogeneous microstructure (Fig. 1f), compared to the other cases utilizing nanometer SDC powder (Fig. 1b and d). Some defects larger than 1 μm were observed on the surface of single coated SSZ/SDC-1 (Fig. 1b); the uniformity of SDC interlayer was improved by double coating the SDC film (Fig. 1d). It should be mentioned that the SDC slurry was not yet optimized. The composition of slurry for the SDC powder was similar to that of the GDC slurry, of which organic additives were optimized for a fine ceramic powder, but not for a nanometer one like the adopted SDC powder. Further optimization of preparing the SDC slurry is under examination. Fig. 1g and h show magnified surface views of SDC and GDC interlayers.
respectively. Both interlayers show a good particle-to-particle contact. However, openings in SDC interlayer were larger than those of GDC interlayer.

| Temperature | SSZ/SSC | SSZ/SDC-1/SSC |
|-------------|---------|----------------|
| 1100°C     | •       | •              |
| 1000°C     | •       | •              |
| 900°C      | •       | •              |
| SSC        | •       | •              |
| SSZ        | •       | •              |

| Temperature | SSZ/SDC-2/SSC | SSZ/GDC/SSC |
|-------------|---------------|-------------|
| 1100°C     | •             | •           |
| 1000°C     | •             | •           |
| 900°C      | •             | •           |
| SSC        | •             | •           |
| SDC        | •             | •           |
| SSZ        | •             | •           |

**Figure 2.** XRD spectra for SSC film deposited on several substrates such as SSZ (a); SSZ/SDC-1 (b); SSZ/SDC-2 (c); and SSZ/GDC (d); • shows peaks of generated SrZrO$_3$. Fig. 2 shows XRD spectra for SSC thin films deposited on a SSZ disk and doped ceria films of various SSZ disk/ doped ceria film systems. The spectra of SSZ, SSC and doped ceria powders are also included for reference. For the case of SSZ/SSC, Fig. 2a, a reaction was clearly observed at 1000°C, and it developed further at 1100°C. The major reaction product formed at the interface was SrZrO$_3$. However, in cases of SSZ/SDC-1/SSC (Fig. 2b) and SSZ/SDC-2/SSC (Fig. 2c), formation of SrZrO$_3$ was only
observed after calcination at 1100°C. For the SSZ/GDC/SSC system (Fig. 2d), no second phases were detected even after calcination at temperatures as high as 1100°C. These results indicate that the thin films of doped ceria prepared from nanometer SDC and micrometer GDC powders by the wet ceramic process adopted in this study may have beneficial effects for using SSC as a cathode material on stabilized zirconia electrolyte.

![Complex impedance plots of SSC cathodes on various substrates.](image)

**Figure 3. Complex impedance plots of SSC cathodes on various substrates.**

Shown in Fig. 3 are the impedance spectra obtained between 600 and 800°C for SSC cathodes prepared at 950°C on various substrates. Fig. 3a depicts the spectra of a SSC cathode directly deposited on SSZ substrate. Fig. 3b, c, and d compare the spectra of SSC cathodes deposited on SSZ/SDC-1, SSZ/SDC-2, and SSZ/GDC at 600, 700 and 800°C,
respectively. Spectra of the SSC cathode prepared on a dense GDC disk are also given in Fig. 3b, c, and d. All plots showed single depressed arcs; the arcs provide interfacial resistance \((R_a)\) of SSC cathode. The intercepts of the impedance arcs with the real axis at high frequencies correspond to the ohmic resistance \((R_b)\). At a certain temperature, both the ohmic resistances \((R_b)\) and the interface conductivities \((\sigma_i)\) depend on the structure of substrates in the order of \(R_b, \text{SSZ/GDC/SSC} < R_b, \text{SSZ/SDC-2/SSC} < R_b, \text{SSZ/SDC-1/SSC} < R_b, \text{SSZ/SSC}\) and \(\sigma_i, \text{SSZ/GDC/SSC} > \sigma_i, \text{SSZ/SDC-2/SSC} > \sigma_i, \text{GDC/SSC} > \sigma_i, \text{SSZ/SDC-1/SSC} > \sigma_i, \text{SSZ/SSC}\). The interface conductivity of SSC at 700°C was estimated at 7.2 S/cm² in SSZ/GDC/SSC, 4.4 S/cm² in SSZ/SDC-2/SSC, 3.8 S/cm² in GDC/SSC, 2.0 S/cm² in SSZ/SDC-1/SSC, and 0.05 S/cm² in SSZ/SSC, respectively. The observed tendencies imply that in order to suppress the solid state reaction between cobaltites and stabilized zirconia as well as to improve the performance of SSC cathode, controlling the microstructure of doped ceria interlayers is important. The Arrhenius plots of the interface conductivities are shown in Fig. 4. The activation energy of SSC on SSZ/doped ceria films was ca.1.3 eV, smaller than that of SSC prepared on SSZ electrolyte (1.8 eV). The interface conductivity achieved in this study was better than that of a \((\text{Sm}_{0.6}\text{Sr}_{0.4})\text{CoO}_3\), \(\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}\), and Ag composite cathode, which was attached directly on SSZ electrolyte by firing at a temperature as low as 850°C to avoid solid state reactions: 1.7 S/cm² at 700°C with the activation energy of 1.5 eV (9).

![Figure 4. Arrhenius plots of the interface conductivity for SSC cathode prepared on several of substrates such as SSZ (•), GDC (○), SSZ/SDC-1 (△), SSZ/SDC-2/SSC (○), and SSZ/GDC (□).](image)

Fig. 5 shows the cathodic overpotentials measured on SSC cathode. The overpotentials of SSC directly prepared on SSZ were very large, due to the poor chemical compatibility between SSC and SSZ. By introducing a doped ceria interlayer, the cathodic reaction of SSC improved. The performance of SSC prepared on the double coated SDC interlayer was equivalent with that of SSC deposited on a dense GDC substrate, while SSC
prepared on SSZ electrolyte coated by GDC interlayer gave even better performance.

![Graph of Overpotential curves at 600°C and 700°C](image)

**Figure 5.** Overpotential curves of SSC cathode prepared on several substrates such as SSZ (∗), GDC (○), SSZ/SDC-1 (∆), SSZ/SDC-2 (○), and SSZ/GDC (□).

**CONCLUSIONS**

Usage of SSC as cathode material on SSZ electrolyte SOFCs was realized by adopting a thin film of doped ceria as a protective layer for preventing the solid state reaction between the cathode and electrolyte. Thin and uniformly doped ceria films were successfully prepared by a traditional wet ceramic process using submicrometer or nanometer material powders. The results of XRD and electrochemical characterizations show that the prepared interlayers were not only effective in preventing SSC reaction with SSZ electrolyte, but also improved the cathodic reaction of SSC. The microstructure of the interlayer strongly affects its function. The SSC cathode deposited on SSZ electrolyte coated by SDC or GDC interlayer can reach an interface conductivity of 4.4 S/cm² or 7.2 S/cm² at 700°C, respectively.

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