A STUDY OF LOW TEMPERATURE CATHODES ON SSZ ELECTROLYTE

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ABSTRACT

Performance of a Sm$_{0.6}$Sr$_{0.4}$CoO$_3$-YSZ-Ag and a Sm$_{0.6}$Sr$_{0.4}$CoO$_3$-CYO-Ag mixture cathode on Sc$_0$Zr$_{0.89}$Ce$_{0.01}$O$_{1.95}$ (SSZ) electrolyte was studied by the 3-terminal AC impedance method combined with DC component, instead of the traditional I-V curve measurement. The Cole-Cole plot of AC impedance showed a change of electrode/electrolyte interfacial resistance with the over-potential. The sintering temperature of the electrode is determined by examining the reaction temperature between Sm$_{0.6}$Sr$_{0.4}$CoO$_3$ and SSZ. It is found that higher sintering temperature leads to larger interfacial resistance, Sintering at 850°C results in an interface conductivity of over 1S/cm$^2$ at 700°C, with normal activation energy.

INTRODUCTION

Reduction of the operation temperature of solid oxide fuel cells (SOFCs) is important for the commercialization of this technology. A lower temperature enables utilization of metallic materials and helps to extend the life of the cell. However, at low temperatures, the traditional electrode materials, for example La$_{x}$Sr$_{1-x}$MnO$_3$, cannot give satisfactory performance. Potential candidates for cathode materials for low temperatures are Ln$_{1-x}$Sr$_x$CoO$_3$ (Ln=La, Pr, Sm, Gd, etc.), the perovskite-type complex oxides of rare earth elements and cobalt which show very high electronic conductivity and high ionic conductivity over a large temperature range (1, 2). The high ionic conductivity guarantees much broader active sites than La$_{x}$Sr$_{1-x}$MnO$_3$, leading to higher performance.

The performance of La$_{0.6}$Sr$_{0.4}$Co$_3$O$_{2.9}$Fe$_{0.1}$O$_3$ on ceria electrolyte (3,4), Sm$_{0.5}$Sr$_{0.5}$Co$_3$ on LaGaO$_3$-based electrolyte (5) and Gd$_{0.5}$Sr$_{0.5}$CoO$_3$ on YSZ (6) has been studied in detail and
good results achieved. The effects of ceria addition (7) and Pt dispersion (8) have also been positive. We also studied a mixture cathode of Ce0.8Gd0.2O1.9, La0.6Sr0.4Co0.8Fe0.2O3 and Ag on Ce0.8Sm0.2O1.9 electrolyte (9) and found it can give good performance. This motivated us to study the performance of similar cathode structure on Sc0.1Zr0.89Ce0.01O1.95 (SSZ, scandia-stabilized zirconia). SSZ has twice to triple the ionic conductivity of YSZ (yttria stabilized zirconia) and has much higher strength than doped ceria (10), so that it is a very attractive candidate for electrolyte for low temperature SOFCs.

Although it is well known that Sr-doped rare earth cobaltite has problems such as large thermal expansion coefficient and high reactivity with zirconia based electrolyte, the problems do not seem to be severe for low temperature operation. However, high temperature sintering must be avoided. Of course, to build the cathode/electrolyte structure by sputtering, laser ablation or vapor deposition is effective to avoid the solid reaction. To reduce the cost, however, low temperature sintering below the reaction temperature is worthy of investigation.

In the present work, we explore low temperature sintering and examine the performance of cathodes with Sm0.6Sr0.4CoO3 (SSC) as the main component, YSZ or CYO (Ce0.8Y0.2O1.9) as sintering aid, and Ag as auxiliary component to improve the surface exchange reaction of oxygen. It was confirmed that SSC reacts with SSZ at temperatures higher than 900°C. By sintering the cathode/electrolyte structure at 850°C, interface conductivity over 1 S/cm² at 700°C, with normal activation energy, was achieved.

**EXPERIMENTAL**

As the starting materials, Sm2O3, SrCO3, and 2CoCO3.3Co(OH)2.4H2O were used. Sm2O3 was calcined at 1200°C to remove any hydroxide, and carbonate, SrCO3 was dried at 120°C. The real Co content in 2CoCO3.3Co(OH)2.4H2O was analyzed by heating it to complete decomposition at 700°C and weighing the obtained Co3O4. After the starting materials were weighed as required, they were dissolved into nitric acid and the solutions were mixed.

For preparation of SSC, the coprecipitation method was used. The mixed solution was dropped into a solution of ammonium oxalate to carry out coprecipitation. After filtration, however, it was found that the stock had a light pink color, showing that the precipitation of Co²⁺ was not complete; so the stock was heated to dry up and the remains were added to the precipitation, which was decomposed at 700°C to get a precursor of SSC. The powder obtained was ball milled and calcined at 1000°C, then examined by X-ray diffraction.
The reactivity of the obtained powder with SSZ was examined by mixing it with the SSZ powder, firing the mixture at various temperatures, then measuring the X-ray diffraction patterns. Mixing was done in a YSZ ball mill for 24 hrs and calcination was carried out at 800, 900, 1000, and 1100°C, for 3 hrs separately.

To sinter the SSC powder obtained at 1000°C, at as low a temperature as 850°C, it was necessary to add a sintering aid. The sintering aid must be compatible with both the cobaltite and the electrolyte, mechanically, chemically and electrochemically. The fine powder of electrolyte itself, when it is fine enough and can be sintered at a low temperature before reaction with SSC, should be the best choice for this purpose. From this viewpoint, the mixed solution of related octoates (2-ethylhexoates) was selected. Two kinds of mixed solutions were prepared, one for the expected composition as Ce0.8Y0.2O1.8 (CYO), another was for (Y2O3)0.8(ZrO2)0.92 (YSZ). Both solutions were mixed with the SSC powder in a ball mill to get slurries, which were screen printed on to pellets of the SSZ electrolyte and followed by sintering. The weight ratio of CYO/SSC was controlled as 1/10 while that of YSZ/SSC was 3/7. A Ni-ceria anode was prepared on the opposite side of the electrolyte pellets beforehand. After sintering, the cathodes were coated by AgNO3, followed by heat decomposition and firing at 750–800°C for 3 hrs.

The performance of the CYO-SSC-Ag cathode and the YSZ-SSC-Ag cathode was measured by a 3-probe complex impedance method at steady states of DC current. A Pt reference electrode was set on the side of the electrolyte pellet; a glass-free Pt paste (Tanaka Kikinzoku Co. Japan) was used for this purpose.

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction patterns of the SSC powder (a) and of a mixture of SSC with 50w% SSZ (b). The SSC powder prepared by coprecipitation method and calcined at 1000°C was a perovskite phase. As for the mixture, the diffraction pattern after calcination at 800°C was the same as that obtained at room temperature, showing that no reaction occurred below 800°C. Calcination at 900°C, however, resulted in peaks such as SrZrO3 and Co3O4. Calcination at 1100°C resulted in peaks of SrZrO3, Sm2Zr2O7 and Co3O4. The peaks of the products became much stronger than of the reactants after calcination at 1100°C.

Fig. 2 shows the SEM image of the SSC powder and the surface of the YSZ-SSC-Ag cathode. The SSC powder (Fig. 2, a) was fine; the particle radius being less than 1μm. The surface of the YSZ-SSC-Ag cathode (Fig. 2, b, c) shows that YSZ from octoates was well sintered at as low a temperature as 850°C. However, the shrinkage of the YSZ-SSC-
Ag cathode was too severe; the stress caused by this shrinkage may hinder the sintering of the cathode to the surface of the electrolyte. As a result, the cathode was easy to peel after the performance test. It was found that higher the sintering temperature the stronger the contact of the cathode to the electrolyte. However, because of the solid state reaction, a high sintering temperature is not preferred.

The surface and the cross section of the CYO-SSC-Ag cathode (Fig. 3 a, b, c) show a good structure for an electrode. The porosity is sufficient and the electrode is not divided into narrow sections as the YSZ-SSC-Ag cathode. Contact of the CYO-SSC-Ag cathode to the electrolyte was stronger than the YSZ-SSC-Ag cathode.

Fig. 4 shows the Cole-Cole plots of the CYO-SSC-Ag cathode at various temperatures. The arc on the high frequency side is confirmed to correspond to the grain boundary of the electrolyte. This arc also occurs for Pt cathode and for the YSZ-SSC-Ag cathode. The high frequency arc is further found to become larger at lower temperatures but to be independent of the current density. The interface conductivity of the CYO-SSC-Ag cathode at 700°C is about 1.7 S/cm² at open circuit state. The Arrhenius plot of the interface conductivity is shown in Fig. 5, the activation energy was obtained as 1.5 eV.

Fig. 6 shows the polarization curves of the YSZ-SSC-Ag cathode sintered at different temperatures. The sintering temperature is found to be an important factor in the performance. The higher the sintering temperature, the worse the performance. This fact coincides with the reactivity between SSC and SSZ. Sintering at 850°C results in an interface conductivity greater than 1S/cm² at 700°C.

The polarization curves of the YSZ-SSC-Ag cathode, the CYO-SSC-Ag cathode and the Pt paste cathode are compared in Fig. 7. The Pt paste was the same as mentioned for the reference electrode. The interface resistance of the Pt paste cathode was very large, showing that Pt cathode does not give satisfactory performance under this condition. The CYO-SSC-Ag cathode shows the best performance in Fig. 7. However, further improvement in performance is needed for practical applications. For further work, it seems necessary to optimize the CYO/SSC ratio and the sintering temperature. From the viewpoint of the ionic conductivity of the materials, use of Sm-doped ceria (CSO) instead of CYO and adjustment of the Sr amount of SSC should improve the performance.

CONCLUSIONS

Using fine powders of doped ceria or zirconia, obtained from on site decomposition of metal-organic compounds, it is possible to sinter SSC based cathode onto the SSZ
electrolyte at as low a temperature as 850°C to avoid solid state reactions. The cathode
obtained by such method, after Ag coating, can reach an interface conductivity of over
1S/cm² at 700°C in air.

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Fig. 1 X-ray diffraction patterns of the SSC powder calcined at 1000°C, and of its mixture with SSZ powder calcined at various temperatures.

a. The SSC powder calcined at 1000°C

b. Mixture of SSC and SSZ

$x = \text{Sm}_2\text{Zr}_2\text{O}_7$

$y = \text{Co}_3\text{O}_4$

$z = \text{SrZrO}_3$
Fig. 2 SEM image of the SSC powder (a) and of the YSZ-SSC-Ag cathode (b, c).

a. Sm$_{0.6}$Sr$_{0.4}$CoO$_3$ powder

b. Surface of the YSZ-SSC-Ag cathode

c. Cracks on the surface of the YSZ-SSC-Ag cathode
a. Surface of the CYO-SSC-Ag cathode

b. Cross-section of the CYO-SSC-Ag cathode

c. Cracks on the surface of the CYO-SSC-Ag cathode

Fig. 3 SEM image of the CYO-SSC-Ag cathode.
Fig. 4 Cole-Cole plots at various temperatures for the CYO-SSC-Ag cathode.

Fig. 5 Arrhenius plot of the interface conductivity for the CYO-SSC-Ag cathode.

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Fig. 6 Polarization curves for the YSZ-SSC-Ag cathode sintered at various temperatures.

Fig. 7 Polarization curves for the CYO-SSC-Ag cathode, the YSZ-SSC-Ag cathode, and the Pt paste cathode.