Investigation of LSM$_{1.1}$–ScSZ composite cathodes for anode-supported solid oxide fuel cells

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Abstract

La$_{0.8}$Sr$_{0.2}$Mn$_{1.1}$O$_3$ (LSM$_{1.1}$)–10 mol% Sc$_2$O$_3$-stabilized ZrO$_2$ co-doped with CeO$_2$ (ScSZ) composite cathodes were investigated for anode-supported solid oxide fuel cells (SOFCs) with thin 8 mol% Y$_2$O$_3$-stabilized ZrO$_2$ (YSZ) electrolyte. X-ray diffraction (XRD) results indicated that the ScSZ electrolytes displayed good chemical compatibility with the nonstoichiometric LSM$_{1.1}$ against co-firing at 1300 °C. Increasing the CeO$_2$ content in the ScSZ electrolytes dramatically suppressed the electrode polarization resistance, which may be related to the improved surface oxygen exchange or the enlarged active area of cathode. The 5Ce10ScZr was the best electrolyte for the composite cathodes, which caused a small ohmic resistance decrease and the reduced polarization resistance and brought about the highest cell performance. The cell performances at lower temperatures seemed to rely on the electrode polarization resistance more seriously than the ohmic resistance. Compared with the cell impedance at higher temperatures, the higher the 5Ce10ScZr proportion in the composite cathodes, the smaller the increment of the charge transfer resistance at lower temperatures. The anode-supported SOFC with the LSM$_{1.1}$–5Ce10ScZr (60:40) composite cathode achieved the maximum power densities of 0.82 W/cm$^2$ at 650 °C and 2.24 W/cm$^2$ at 800 °C, respectively.

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1. Introduction

Anode-supported solid oxide fuel cells (SOFCs) with thin 8 mol% yttria-stabilized zirconia (YSZ) electrolyte have achieved maximum power densities of 1.9 W/cm$^2$ at 800 °C [1]. Higher power density could also been attained by using the functionally graded electrodes. Due to the excellent power generation characteristics, anode-supported SOFCs with thin YSZ electrolyte lead the developments of intermediate-temperature SOFCs (IT-SOFCs, operated between 650 and 800 °C). In this type of cells, the YSZ film is around 10–20 μm in thickness and contributes a minor ohmic resistance in a cell compared with that of the electrolyte-supported cells. So, it becomes less necessary for the cell performance improvement through further reducing the electrolyte thickness. State-of-the-art porous Ni–YSZ anode substrate brings about negligible polarization loss with a thickness of 1 mm. It is generally regarded that the polarization loss from Sr-doped LaMnO$_3$ (LSM)–YSZ composite cathode is the key issue for the further improvement in cell performance [1].

LSM–YSZ composite cathode was firstly reported by Kenjo and Nishiya [2] and excellently reviewed by Alder [3] and Fleig [4]. The same two means for optimization can also be employed to achieve an improved cathode performance: (a) geometrical parameters (e.g., porosity and particle size) can be varied and, in particular for composite cathodes, the size, volume fraction, and spatial distribution of electrolyte and electrode particles can be optimized and (b) materials’ properties may be improved, e.g., by modifying the dopant ion or dopant concentration or by switching to other materials systems. Besides the gradual
engineering optimization of the cathode structure, two approaches are under endeavoring to improve the electrochemical activity of LSM–YSZ. One way is to introduce a doped ceria layer, such as Y2O3-doped CeO2 (YDC) layer, between the LSM–YSZ cathode and the YSZ electrolyte film because the surface oxygen exchange coefficient of YDC electrolyte is much higher than that of the YSZ one [5]. In practice, the ceria interlayer is usually fabricated through some expensive processes, such as chemical vapor deposition, in order to avoid the detrimental diffusion of Ce element into YSZ under high temperature [6,7]. The ceria interlayer would also increase the complexity of cell structure and the fabrication cost and would reduce cell stability due to the difference in thermal expansion coefficients. Therefore, it is suggested that the use of composite electrolyte structure should be subject to extremely careful evaluation and each time a new interface is inserted unforeseen loss mechanisms may arise [8]. An alternative for reducing charge transfer resistance has been proposed, in which the dispersed electrolyte grains of highly conducting 10 mol% Sc2O3-stabilized ZrO2 co-doped with 1 mol% CeO2 (1Ce10ScZr) was implanted on the surface of YSZ thin film [9]. Since the 1Ce10ScZr grain implanting does not bring about an additional layer, the cell can remain a simple tri-layered structure. Another way is to replace the YSZ electrolyte in the LSM–YSZ composite cathode by other electrolytes with higher ionic conductivity, such as Gd2O3-doped CeO2 (GDC), Bi2O3-doped CeO2 (CBO) and doped LaGaO3 (typically La0.9Sr0.1Ga0.8Mg0.2O3, LSGM). It has been found that LSM-GDC composite cathode (50:50, weight ratio) can reduce the interfacial resistance to less than a half [10]. The direct impregnation of the LSM electrode with Gd0.8Ce0.2(NO3)3 solution can reduce the electrode polarization resistance as small as 0.72 V at 700 °C, which seems much better than that of LSM–YSZ and LSM–GDC electrodes [11]. Because of the comparable ionic conductivity of Ce0.7Bi0.3O2 and GDC, similar results are obtained with the LSM–Ce0.7Bi0.3O2 composite cathode [12,13]. The LSM–LSGM composite cathode has also been investigated for the anode-supported SOFCs with YSZ thin film [14], but due to the reactions between LSGM and YSZ electrolyte above 1000 °C, it is difficult to fire the LSGM–LSM composite cathode onto the YSZ electrolyte without reactions.

Sc2O3-stabilized ZrO2 co-doped with CeO2 (ScSZ) exhibits the same thermal expansion coefficient and good chemical compatibility with YSZ. More importantly, ScSZ displays a much higher oxygen ionic conductivity than the YSZ electrolyte. Accordingly, Pt (Ag)–ScSZ cathodes were developed for and successfully applied in intermediate-temperature SOFCs [15,16]. In this paper, the LSM1.1–ScSZ composite cathodes were investigated for anode-supported SOFCs with the YSZ thin film. The effects of the CeO2 doping content in ScSZ electrolytes, the ScSZ content in the composite cathodes and the firing temperature on the cell performances were evaluated.

2. Experimental

2.1. Preparation of anode/electrolyte assemblies

YSZ powder from Tosoh Corporation and nickel oxide (NiO) from J. T. Baker Corporation were mixed in a weight ratio of 1:1 with a pestle in an agate mortar. Anode substrate was fabricated via a tape-casting process with suitable organic binders and n-butanol solvent. YSZ colloidal suspension was supported on the anode substrate by slurry coating method. The anode/electrolyte assemblies obtained were drilled into discs and pressed uniaxially under 94 MPa. The discs were then sintered at 1400 °C for 2 h in air. The anode/electrolyte assemblies were about 20 mm in diameter and 600 μm in thickness. The thickness of the YSZ electrolyte film was ca. 15 μm.

2.2. Fabrication of composite cathodes

La0.8Sr0.2Mn1.1O3 (LSM1.1) was adopted as cathode electrocatalyst. La2O3 (A.R. 99%), Sr(NO3)2 (A.R. 99.5%) and Mn(NO3)2 aqueous solution (A. R. 49–51%) were used as starting materials. LSM1.1 powder was synthesized through the combined citrate and EDTA complexing method [17] and calcined at 1100 °C for 2 h to form pure perovskite phase and suitable particle size distribution. The electrolytes of Sc2O3-stabilized ZrO2 co-doped with CeO2 were prepared through chemical co-precipitation. Three ScSZ electrolytes of (Sc2O3)0.10−(ZrO2)0.90−(CeO2)0.01, (Sc2O3)0.10−(ZrO2)0.85−(CeO2)0.05 and (Sc2O3)0.10−(ZrO2)0.80−(CeO2)0.10 were named hereafter as 1Ce10ScZr, 5Ce10ScZr and 10Ce10ScZr, respectively. The LSM1.1–ScSZ composite cathodes were screen-printed on the electrolyte surface and fired at different temperatures for 2 h in air. The coin cathode as prepared had an effective area of about 0.5 cm2 and a thickness of about 50 μm.

The constriction effect on cell performance as frequently observed not only occurred at the electrode/electrolyte interface but also at the cathode/current collector interface [18]. So, Ag paste was painted on the cathode surface before cell testing to improve current collecting [19].

2.3. Cell testing

A homemade apparatus was used for the cell performance test. Ag meshes were adopted as current collectors. Silver wires welded on Ag meshes were used in anode and cathode chambers as both current probe and voltage one, which experimentally produced a slightly decreased performance due to the voltage loss originated from the Ag wire resistance.

Humidified hydrogen, through bubbling from water at room temperature, was fed into the anode and pure O2 was fed into the cathode as oxidant gas. Both gases were kept at the same flow rate of 75 ml/min by mass flow controllers. Since the polarization impedance of LSM electrode was
greatly influenced by the electrochemical history \cite{20,21},
the cell was electrically loaded at 800 °C and 0.7 V for 0.5 h
to activate LSM–ScSZ composite cathode before the
performance measurement. The cell voltage and the
corresponding current were recorded through varying the
outside electrical load.

2.4. EIS measurements

Two-probe electrochemical impedance spectra (EIS)
were measured by Solartron-1260 frequency responding
analyzer combined with Solartron-1287 electrochemical
interface. The EIS were recorded in a frequency range of
50 kHz to 0.1 Hz with a signal amplitude of 10 mV under
open circuit voltage (OCV). The overall complex impe-
dance data were fitted by a complex non-linear least square
(CNLS) fitting program in ZView2.8 software.

2.5. XRD measurements

XRD patterns were used to analyze the chemical
compatibilities against high temperature. LSM$_{1.1}$ and ScSZ
mixtures were cured at different temperatures between 1000
and 1300 °C and the XRD patterns of pure LSM$_{1.1}$ and
cathodic mixtures were taken using a Rigaku miniflex
diffactometer.

3. Results and discussion

3.1. XRD

Fig. 1a illustrates the XRD patterns of the mixtures of
LSM$_{1.1}$ and different ScSZ electrolytes after they were
calcined at 1200 °C. Pure LSM shows a single-phase cubic
perovskite structure, whereas the LSM$_{1.1}$–ScSZ mixtures
show binary patterns of cubic perovskite phase of LSM$_{1.1}$
and cubic structure of ScSZ. It is generally accepted that
solid-state reactions between stoichiometric LSM with Sr
content over 0.3 in A-site and YSZ easily occur at above
1200 °C and result in high-resistance phase of La$_2$Zr$_2$O$_7$
\cite{22}. The La$_2$Zr$_2$O$_7$ impurity seriously interferes with the
surface diffusion of O$_{ad}$ from the LSM surface to the three-
phase boundary (TPB) \cite{23} and in turn increases the
cathodic polarization loss \cite{24}. Since La$_2$Zr$_2$O$_7$ are formed
whenever the diffusion of Mn into YSZ leaves chemically
active La$_2$O$_3$ at the interface LSM/YSZ \cite{25} and the
nonstoichiometric compound LSM$_{1.1}$ with B-site excessive
perovskite can suppress the reactions \cite{24–26}, the cathodic
electrocatalyst LSM$_{1.1}$ other than the stoichiometric LSM is
used in this study. The diffraction peaks for the La$_2$Zr$_2$O$_7$
pyrochlore phase is not observed in these mixtures. Even
after being calcined at 1300 °C, the La$_2$Zr$_2$O$_7$ is not detected
from the LSM$_{1.1}$–5Ce10ScZr mixtures, as shown in Fig. 1b.
So, LSM$_{1.1}$ and ScSZ show good chemical compatibility
against the accustomed curing temperatures.

3.2. Effect of ScSZ electrolytes

The cell impedance spectra reflect the electrode polariza-
tion impedances both from anode and cathode. Leng et
al. has proposed a simple equivalent circuit to discriminate
the impedance contributions from different processes \cite{27}.
Since the contribution of anode polarization is much smaller
than that of cathode, by virtue the electrode resistance of the
cell is mainly due to cathode polarization. Two suppressed
arcs can be discriminated in the impedance spectra. The
small arc in high-frequency region is mainly attributed to the
charge transfer of oxygen ions from the composite cathode
to the YSZ electrolyte and the large one in low-frequency
region indicates the dissociative adsorption and/or surface
diffusion processes. Other processes can also contribute
some small portions to the whole spectra, such as the
electrochemical oxidation of hydrogen on anode and the
YSZ grain boundary. To minimize the differences from
anode and electrolyte between different cells, the anode/electrolyte assemblies were fabricated in batch processes under the same conditions. Before the evaluation of the new composite cathodes, the cells with the same batch of anode/electrolyte assemblies and the LSM$_{1.1-}$YSZ composite cathode were tested for at least twice to assure the reproducibility. So, the differences in the cell performance and impedance between different cells can be ascribed to the contributions of the composite cathodes.

Fig. 2 shows the EIS of the LSM$_{1.1-}$ScSZ composite cathodes with different ScSZ electrolytes and the evaluated impedance parameters are listed in Table 1. The LSM$_{1.1-}$ScSZ composite cathodes are fixed in the ScSZ proportion of 40 wt.\% because the addition of up to 40 wt.\% YSZ to the cathode can improve the performance because of a better adhesion to the base electrolyte and to the increase of the TPB length [23]. It is found that the total ohmic resistance slightly increases with the doped CeO$_2$ content in the ScSZ electrolytes. The ionic conductivity of ScSZ electrolytes decreases with the doped CeO$_2$ content because the larger Ce$^{4+}$ than Zr$^{4+}$ in ionic radii can produce obvious steric-blocking effect on the oxygen ion migration through lattice vacancy [28,29]. Therefore, the increase of ohmic resistance is apparently related to the ionic conductivities of the ScSZ electrolytes.

Fig. 2 also shows that the low-frequency arc for surface diffusion and the high-frequency one for charge transfer are related to the ionic conductivities of the ScSZ electrolytes. Therefore, the increase of ohmic resistance is apparently related to the ionic conductivities of the ScSZ electrolytes.

Table 1

<table>
<thead>
<tr>
<th>LSM$_{1.1-}$</th>
<th>LSM$_{1.1-}$</th>
<th>LSM$_{1.1-}$</th>
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<tbody>
<tr>
<td>1Ce10ScZr</td>
<td>5Ce10ScZr</td>
<td>10Ce10ScZr</td>
</tr>
<tr>
<td>$R_o$ ((\Omega) cm$^2$)</td>
<td>0.120</td>
<td>0.123</td>
</tr>
<tr>
<td>$R_1$ ((\Omega) cm$^2$)</td>
<td>0.093</td>
<td>0.073</td>
</tr>
<tr>
<td>$R_2$ ((\Omega) cm$^2$)</td>
<td>0.444</td>
<td>0.385</td>
</tr>
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</table>

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In conclusion, the surface oxygen exchange characteristics other than the bulk conductivities of the ScSZ electrolytes may be responsible for the reduction of the electrode polarization resistance.

Figs. 3a and 3b show the cell performances with different composite cathodes and the evaluated impedance parameters are listed in Table 1. The LSM$_{1.1-}$ScSZ composite cathodes with the same batch of anode/electrolyte assemblies and the LSM$_{1.1-}$YSZ composite cathode were tested for at least twice to assure the reproducibility. So, the differences in the cell performance and impedance between different cells can be ascribed to the contributions of the composite cathodes.

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3.3. Effect of cathode firing temperature

Firing temperature is a critical parameter for a cathode to obtain suitable porosity, long TPB, tight adhesion to the electrolyte surface and close electrical and physical connection between LSM and ScSZ. Fig. 4 gives the cell performances with firing temperatures between 1000 and
1300 °C and Fig. 5 gives the ohmic resistances at 800 °C with the cathodes fired at different temperatures. The cathode fired at 1100 °C brings about the best cell performance. At a firing temperature of 1000 °C, a large ohmic resistance resulted. The cathode/electrolyte interfacial adhesion is so incompact that the cell performances are suppressed significantly. With the firing temperature increased to 1100 °C, the ohmic resistance is lowered to 0.11 Ω cm² and the cell achieves the highest MPD of 2.24 W/cm². With further increasing of the temperature, the ohmic resistance exhibits slow increases accompanying slightly decreased cell performances. But the cell performances are obviously higher than that of the cells with the cathode fired at 1000 °C. The incompact interfacial adhesion from lower firing temperature seems to destroy the cell performance more seriously than the shortened TPB length from higher temperature, which is also the case for the La₀.₉Sr₀.₁MnO₃–YSZ composite cathode [33].

3.4. Effect of 5Ce10ScZr proportion

Fig. 6a shows the cell performances at 800 °C with varying the 5Ce10ScZr proportion from 20 to 50 wt.%. When the 5Ce10ScZr proportion is below 40 wt.%, the increase of the 5Ce10ScZr proportion leads to the gradual increase of the cell performances. The cathode with 50 wt.% 5Ce10ScZr, however, brings about slightly decreased cell performance. At 800 °C, the cathode with 40 wt.% 5Ce10ScZr is the best one while the cathode with 50 wt.% 5Ce10ScZr is the worst one. Fig. 6b gives the cell performances at 650 °C, in which the cathode with 40 wt.% 5Ce10ScZr brings about the best performance with an MPD of 0.82 W/cm². Dissimilarly, not the cathode with 50 wt.% 5Ce10ScZr but the one with 20 wt.% 5Ce10ScZr results in the worst performance at 650 °C.

Fig. 7 gives the EIS at 800 °C of the cells with different cathode compositions. The cathode containing 30 wt.% 5Ce10ScZr results in the smallest ohmic resistance of 0.100 Ω cm², which is mainly determined by the optimization of the cathode/electrolyte interface. When the 5Ce10ScZr
proportion increases to 50 wt.%, the cathode would suffer from the partial discontinuity of the electronic conducting phase and shows an increased ohmic resistance of 0.16 \( V \) cm\(^2\), which is obviously higher than that for the cells with 30–40 wt.% 5Ce10ScZr. In the meantime, the excess 5Ce10ScZr in the composite cathode reduces the TPB length and, in turn, the slight increase of the electrode polarization resistance.

The impedance arc for the surface diffusion processes would be drastically suppressed under current loading while the high-frequency one for the charge transfer processes would be nearly unaffected \([27,34]\). Therefore, the charge transfer resistance is a key factor limiting the cell performance. The composite cathodes with different 5Ce10ScZr proportions show different temperature dependences of the charge transfer resistance. Table 2 lists the corresponding activation energies between 650 and 800 °C for the composite cathodes with different 5Ce10ScZr proportion.

The activation energy of the composite cathode with 20 wt.% 5Ce10ScZr is 96 kJ/mol, which is already lower than the corresponding value 107 kJ/mol for the LSM cathode on YSZ substrate \([35]\). The activation energy decreases gradually with the 5Ce10ScZr proportion and reaches a minimum of 44 kJ/mol of the cathode with 50 wt.% 5Ce10ScZr. The higher 5Ce10ScZr proportion, the smaller increase of the charge transfer resistance when operation temperature decreases. Accordingly, the cathode with 50 wt.% 5Ce10ScZr shows a much

<table>
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<tr>
<th>LSM : 5Ce10ScZr weight ratio</th>
<th>Activation energy (kJ/mol)</th>
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<tr>
<td>50 : 50</td>
<td>44</td>
</tr>
<tr>
<td>60 : 40</td>
<td>58</td>
</tr>
<tr>
<td>70 : 30</td>
<td>75</td>
</tr>
<tr>
<td>80 : 20</td>
<td>96</td>
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smaller charge transfer resistance and a much higher performance than the one with 20 wt.% 5Ce10ScZr at 650 °C, as demonstrated by Figs. 7 and 6b.

4. Conclusions

$\text{LSM}_{1.1}$–5ScSZ composite cathodes were investigated for the anode-supported solid oxide fuel cells with thin YSZ electrolyte. The Mn excess in the B-sites of $\text{LSM}_{1.1}$ perovskite suppressed the solid-state reactions between $\text{LSM}_{1.1}$ and ScSZ under the accustomed firing temperatures. The increase of CeO$_2$ content in ScSZ electrolytes may improve the surface oxygen exchange and enlarge the effective area for electrode reaction. So the electrode polarization resistances were drastically reduced. With the 5Ce10ScZr proportion increasing from 20 to 50 wt.%, the activation energy of the charge transfer resistance gradually decreased from 96 to 44 kJ/mol. Higher 5Ce10ScZr proportion resulted in higher cell performance at 650 °C. The anode-supported SOFC with the $\text{LSM}_{1.1}$–5Ce10ScZr (60:40) composite cathode achieved the maximum power densities of 0.82 W/cm$^2$ at 650 °C and 2.24 W/cm$^2$ at 800 °C, respectively.

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