PERFORMANCE OF (La, Sr)(Cr, Mn)O3 ANODE FOR DIRECT OXIDATION OF METHANE IN SOLID OXIDE FUEL CELL

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ABSTRACT

The pervoskite material, La0.75Sr0.25Cr0.5Mn0.5O3 (LSCM), was synthesized through solid-state reactions and successfully applied as anode in solid oxide fuel cell for direct oxidation of methane. Optimum sintering temperature of 1200°C was found for the LSCM/YSZ composite anode (50 wt% LSCM/50 wt% YSZ). Although the performance of the composite anode is lower than a Ni/YSZ anode, it exhibits high stability in methane. No carbon deposition and performance deterioration were observed for the LSCM/YSZ composite anode even if the dry methane was fed into the anode as the fuel. The observed OCV in 3% H2O-97% CH4/Air for LSCM/YSZ/Pt system is much lower than the theoretical value calculated from the equilibrium concentration of the mixture gases, CH4, CO, CO2, H2O and H2, implying the slow steam reforming processes of CH4 at LSCM surface. The voltage difference between the experimental and simulation results decreases with the increase of the operating temperature (0.34 V at 750°C and 0.21 V at 950°C) suggesting that the high operating temperature favors the steam reforming processes of CH4 at LSCM surface.

INTRODUCTION

Advances in electroceramics, such as ionic conductors and electronic/ionic mixed conductors, are promoting the development of solid oxide fuel cell (SOFC) technology. The advantages of SOFCs over other kinds of fuel cells reside in: (i) flexible selection of fuels, i.e. hydrogen, natural gas, bio-gas and liquid hydrocarbons; (ii) less electrolyte management problems because of its ceramic components; (iii) tolerant to some poisonous gases, i.e. CO and H2S; and so on. Although hydrogen is almost the best fuel for SOFC to reach high performance, it only can be obtained through reforming of hydrocarbons, electrolysis or photo-electrolysis (1-3). Economically, if possible, it is ideal to directly use hydrocarbons instead of hydrogen as the fuel for solid oxide fuel cell. Methane, as the simplest compound among the hydrocarbons, is one of the most common hydrocarbons studied as the fuel in SOFC due to its abundance on the earth. So far, many researchers have focused on the studies of internal reforming and stability of the SOFC anode in methane fuel (4-8). A major challenge for the direct use of methane in SOFC is to suppress the carbon deposition at the anode.
Nickel is a good anode material for SOFC, but it promotes coke formation when the hydrocarbons are used as fuels. A significant amount of steam must be added in order to prevent coke formation at Ni/YSZ anode, which would dilute the fuel and cause system management problems. Gorte et al. (9-12) published a series of papers about Cu-ceria cermet for direct oxidation of hydrocarbon in SOFC operated at temperature range of 500-700°C. However, from the point view of reliability and system efficiency, the YSZ electrolyte based SOFCs, normally operated at temperature higher than 800°C, are still the most promising for the commercialization. Replacing Ni/YSZ by a nickel-free material with identical electrical and catalytic properties could lead to a significant improvement in long-term stability of SOFC with hydrocarbon as the fuel. Tao and Irvine (13) reported a nickel-free perovskite anode, (La, Sr)(Cr, Mn)O3 (LSCM), which is chemically stable under natural gas or methane and has comparable performance to nickel/YSZ. The efforts of the present study are to further investigate the fabrication process and the performance of LSCM anodes and to primarily understand the oxidation mechanisms of methane at LSCM anodes.

**EXPERIMENTAL PROCEDURE**

The yttria-stabilized zirconia electrolyte (YSZ) was prepared by uniaxially pressing of 10 mol% yttria-stabilized zirconia powder (YSZ, Tosoh Corporation, Japan) with pressure of 50 MPa and sintered at 1550°C for 2 hrs. The La0.75Sr0.25Cr0.5Mn0.5O3 (LSCM) pervoskite powder was synthesized through solid-state reactions. Figure 1 shows the synthesis routine for the La0.75Sr0.25Cr0.5Mn0.5O3 powder. Firstly, La2O3, SrCO3, MnCO3, and Cr2O3 powders were calcined separately at 1000°C for 2 hours to remove moisture.
and impurities. The calcined raw powders were then mixed and ball-milled in a ZrO₂ jar for 4 hours. X-ray diffraction (XRD) pattern indicated the formation of perovskite phase after the powder mixture was sintered at 1200°C for 20 hrs (Fig. 2). The LSCM and YSZ powders were mixed with Polyethylene Glycol 400 to form slurry, screen-printed on the sintered YSZ electrolyte surface and then sintered at 1200°C for 2 hours in air to get the LSCM/YSZ composite anode. The composition of the composite anode was 50 wt% LSCM and 50 wt% YSZ. The thickness of the anode after sintering was around 50 μm and the anode surface area was 0.5 cm². Pt paste was coated on the other side of the YSZ substrate as the counter electrode and reference electrode, followed by sintering at 1100°C for 1 hr. During measurement, the counter and reference electrodes were exposed to the air and the anode was exposed to methane (or hydrogen) atmosphere. The flow rate of methane was set to 100 sccm/min. The anode performance was monitored by an impedance analyzer (Solartron 1287 and 1260, UK) in the frequency range of 0.01-10⁶ Hz. Scanning electron microscopy (SEM, Leica S360) was employed to observe the microstructure of the LSCM/YSZ composite anode.

Figure 2. XRD of the LSCM powder before (a), and after sintering at 1200°C for 20 hrs (b).

RESULTS AND DISCUSSION

The effect of sintering temperature on the impedance spectra of LSCM/YSZ composite anodes is shown in Fig. 3. In order to compare the resistance of the anodes sintered at different temperatures, the ohmic resistance was deducted from the impedance spectra shown in Fig. 3. It is found that 1200°C is the optimum sintering temperature for the LSCM/YSZ composite anode to reach best performance among the three sintering temperatures investigated. Also, with the increase of the sintering temperature, the high frequency arc become more and more dominant, which may be due to the interfacial formation of La₂Zr₂O₇ at LSCM/YSZ interface when the composite anode was sintered at high temperature (14). Fig. 4 shows the microstructure of the composite anodes sintered at different temperatures. The morphology of the composite anode indicates that the high electrode resistance of the anode sintered at 1100°C could be attributed to the poor contact among the grains, leading to insufficient active sites (YSZ and LSCM contact), low ionic conductivity (YSZ and YSZ contact), and low electronic conductivity (LSCM and LSCM contact).
Figure 3 Effect of sintering temperature on the impedance spectra of LSCM anode in humidified CH₄ at 950°C.

Although the grain size of the LSCM does not change much (around 2 μm), the YSZ grains grow significantly from 0.3 μm to 0.9 μm with the increase of the sintering temperature from 1100°C to 1300°C, respectively. To maintain high performance of a

Figure 4. Morphology of LSCM/YSZ composite anodes sintered at (a) 1100°C, (b) 1200°C, and (c) 1300°C after testing.
composite electrode, fine grains and good contact among the grains are both required to ensure sufficient active sites for the reactions and transport of ions (and electrons) between the current collector and electrolyte surface. In the present study case, the high sintering temperature will not only reduce the active sites for the oxidation due to the grain growth but also may cause the formation of passive phase at LSCM/YSZ interface, resulting in low performance of the composite anode sintered at 1300°C.

![Impedance spectra of the LSCM anode as a function of operating temperature](image)

Figure 5. Impedance spectra of the LSCM anode as a function of operating temperature: (a) 750°C; (b) 850°C; 950°C.

The impedance spectra of the LSCM/YSZ composite anode as a function of operating temperature are presented in Fig. 5. No matter hydrogen or methane is used as fuel, three semicircles can be clearly observed from the impedance spectra. Although the results
indicate that the LSCM/YSZ composite anode exhibits poorer performance in humidified CH₄ than in humidified H₂, the composite anode is very stable in CH₄ atmosphere. No carbon deposition and performance deterioration were found for the composite anode even if dry CH₄ was fed into the anode as fuel. It also can be found from Fig. 5 that more performance difference can be observed for the composite anode in humidified CH₄ and H₂ at lower temperature, which may be attributed to the poorer steam reforming of CH₄ at lower temperature. Through fitting the impedance spectra, the electrode resistance of high, intermediate and low frequency arcs can be obtained. And the activation energy of each frequency arc for both humidified H₂ and humidified CH₄ is summarized in Table 1. Much higher activation energy is found in humidified CH₄ than in humidified H₂, which strongly suggests different reaction mechanisms are involved in the composite anode for the oxidation of CH₄ and H₂.

### Table 1. Activation energy for the high, intermediate and low frequency arcs.

|                | High frequency arc | Intermediate frequency arc | Low frequency arc |
|----------------|--------------------|----------------------------|-------------------|
| CH₄            | 149.6 kJ/mol       | 167.6 kJ/mol               | 158.9 kJ/mol      |
| H₂             | 114.6 kJ/mol       | 83.7 kJ/mol                | 102.1 kJ/mol      |

Fig. 6 shows the steady state polarization of the LSCM/YSZ composite anode with humidified H₂ and CH₄ as fuels. Open circuit voltage of 1.14 V and 1.02 V can be reached for 3% H₂O-97% CH₄ and 3% H₂O-97% H₂ at 950°C respectively. Actually, one advantage of the direct use of hydrocarbons is that the Nernst potentials for hydrocarbons are higher than H₂ in the SOFC operating temperature, which could increase the system efficiency. As can be seen in Fig. 6, in the current density range of 0 to 0.25 A cm⁻², higher output power could be obtained in humidified CH₄ than in humidified H₂ due to the higher open circuit voltage, although the overpotential of the composite anode is much higher in humidified CH₄ than in humidified H₂. The overpotential of 0.16 V and 0.08 V at current density of 0.1 A cm⁻² is consistent with the impedance results of 0.078 Ω cm² and 0.175 Ω cm² shown in Fig. 5 in humidified CH₄ and humidified H₂, respectively.
Figure 7. Open circuit voltages (OCV) of the LSCM/YSZ composite anode measured at different temperatures in humidified CH₄ and humidified H₂. The lines are the calculated open circuit for LSCM/YSZ/Pt system in 3% H₂O-97% CH₄/Air and 3% H₂O-97% H₂/Air.

Fig. 7 summarizes the open circuit voltages (OCV) of the LSCM/YSZ composite anode at various operating temperatures in 3% H₂O-97% CH₄ and 3% H₂O-97% H₂. Both the experimental and simulation results are presented in the figure. For LSCM/YSZ/Pt system in 3% H₂O-97% H₂/Air, the OCV slightly drops from 1.1 V at 750°C to 1.02 at 950°C, which is in good agreement with the theoretical OCV calculated from the Nerst equation. However, in 3% H₂O-97% CH₄/Air, the OCV significantly increases from 0.88 V at 750°C to 1.14 V at 950°C. The theoretical OCV in 3% H₂O-97% CH₄/Air was calculated from the equilibrium concentration of the mixture gases, CH₄, CO, CO₂, H₂O and H₂, according to the following four chemical reactions:

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 & \leftrightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
\text{CH}_4 + \text{H}_2\text{O} & \leftrightarrow \text{CO} + 3\text{H}_2 \\
\text{CH}_4 + \text{CO}_2 & \leftrightarrow \text{CO} + 2\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\]

Big voltage difference of 0.34 V at 750°C and 0.21 V at 950°C between the experimental and simulation results was observed, implying slow steam reforming processes of CH₄ at LSCM surface. The voltage difference decreasing with the increase of the operating temperature suggests the high operating temperature favors the steam reforming processes of CH₄ at LSCM surface.
CONCLUSIONS

Pervoskite material, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.3}\text{Mn}_{0.5}\text{O}_3$, was synthesized as SOFC anode through solid-state reactions in this study. The optimum sintering temperature for the LSCM/YSZ composite anode (50wt% LSCM/50wt% YSZ) was found to be 1200°C. The grain size, contact among the grains and the formation of passive phase contribute to the performance of the composite anode. The performance of the LSCM/YSZ composite anode exhibits much poorer performance in humidified CH$_4$ than in humidified H$_2$. The big difference of the activation energy in humidified CH$_4$ and H$_2$ was observed, suggesting the different oxidation mechanisms are involved at the LSCM anode for the oxidation of CH$_4$ and H$_2$. The open circuit voltage of the composite anode in 3% H$_2$O-97% H$_2$/Air agrees well with the theoretical value. However, the observed OCV in 3% H$_2$O-97% CH$_4$/Air is much lower than the theoretical value calculated from the equilibrium concentration of the mixture gases, CH$_4$, CO, CO$_2$, H$_2$O and H$_2$, implying the slow steam reforming processes of CH$_4$ at LSCM surface.

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