

Research on SOFC Properties of Low Concentration Gas Fuel and SFM-GDC Reforming

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Abstract: When gas fuel is used in solid oxide fuel cells, methane cracking occurs at high temperature in the Ni-based anode, forming granular carbon deposition in the active site of the anode, and finally completely wrapped Ni metal, greatly losing the electrochemical performance. Therefore, it is very necessary to add a reforming catalytic layer in the anode of the battery. The methane is reformed into CO and H₂ fuel before entering the anode, and the place where methane cracking occurs is mostly transferred to the reforming layer, which reduces the catalytic reforming burden of the Ni-based anode, so as to effectively improve the battery performance. In this paper, Sr₂Fe_{1.5}Mo_{0.5}O₆ with double perovskite structure was synthesized and prepared, which maintained very good stability in high temperature REDOX atmosphere and had high electrical conductivity. The combination of GDC and SFM can increase the reaction site of the three-phase interface of the reforming layer, and also help to improve the thermal expansion matching between the reforming layer and anode. In this paper, the electrochemical performance of straight cell coated with SSFM-GDC reforming layer has been studied. Low concentration gas in coal mine contains methane, oxygen, nitrogen, and water hydrogen sulfide, etc., and its reaction process in solid oxide fuel cells is complicated. Therefore, studying the reaction mechanism of low concentration gas in solid oxide fuel cells has important practical significance for promoting its application.

1 Introduction

There are three types of support for solid oxide fuel cells. Currently, the main support is anode, which is used to thin the electrolyte and thus reduce the ohmic resistance of the battery. The fuel gas directly passes into the anode of the battery, and thicker anode will affect the diffusion of the fuel gas, resulting in concentration polarization. In order to reduce the concentration polarization of the battery, people have designed a variety of anode microscopic configurations, has been widely reported the traditional dry pressing method anode support body, adding starch and other pore-making agents in the powder, after high temperature sintering, starch volatiles, leaving a porous structure in the anode, but this method of battery anode holes are curved, The diffusion of fuel gases in it has to overcome great resistance, resulting in concentration polarization. In order to solve the problem of concentration polarization, this paper adopts the method of phase conversion and template to prepare the straight hole anode supporting body with regular gradient pore structure, which has important practical significance for the development of high performance SOFC.

2 straight hole cell preparation

In this paper, phase conversion and template were used to prepare anode support cell with straight pore structure. The preparation process was as follows: Firstly, NiO 18.495g, YSZ 12.330g, PVP 0.216g and PESF14.160g were weighed. The preparation process of PESF precursor was as follows: Polyether sulfone resin (PES) and N-methylpyrrolidone (NMP) were mixed in beaks with magnetic force. The above materials were put into the ball mill tank, and the ball mill for 48 hours at the rotating speed of 480r/min to obtain the anode slurry. After the slurry is vacuumized, it is left standing for 12 hours, and then cast into a stainless steel mold to form a disc anode. A stainless steel mesh with a diameter of 150 μm is placed on the surface of the slurry, and a layer of slurry is poured on top of it. The weight is pressed down, and under the action of gravity and the aid of the stainless steel mesh, the upper slurry falls through the aperture of the stainless steel mesh, leaving a straight hole structure in the upper layer. Peripheral water injection (try to inject at even flow rate) wait 2 hours.

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After the samples were taken out, they were soaked in water for 12 hours, and then put in the oven at 50°C for 12 hours, and finally sintered at 1050°C for 2 hours to get the straight hole anode support body.

In order to obtain dense electrolyte, acetone was used as solvent and Hypermer KD-1 as dispersant. The electrolyte powder YSZ was mixed with acetone and KD-1 for 24 h ball milling. After volatilization of acetone, YSZ and GDC slurry was obtained. It needs to be sintered at 400°C for 30 minutes to remove organic matter, repeated three times, and finally sintered at 1400°C for 10 hours to get half a cell.

The GDC barrier layer was further spun onto the YSZ on the half cell and sintered at 1300°C for 5 h. Finally, the cathode paste was prepared. When preparing the electrode paste, the adhesive prepared by the mixture of ethyl cellulose and terpineol (10 wt.%: 90 wt.%) was used, and the powder was mixed and ground. The ratio of powder and terpineol ethyl cellulose was 1:1.5. Finally, on the GDC coated cathode, cathode for round 5 mm in diameter, sintered under 1000 °C for 5 hours, form the structure of NiO - YSZ | YSZ | GDC | LSCF - GDC straight hole support battery anode.

3 Phase structure analysis

The reforming layer of SFM($\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$) was prepared by citric acid-Edta one-step co-sintering method. SFM is a typical double perovskite material. When calcined in air at 1050°C for three hours, a relatively pure

phase is easily obtained. Among them, Fe and Mo at B position can improve the electron conductivity of the battery in REDOX atmosphere [14]. XRD analysis was conducted on the synthesized SFM and GDC materials. The main XRD diffraction peak of SFM material was in good agreement with #43-0645 in the PDF card, belonging to the cubic crystal system double perovskite structure, the space group was Pm3m, and the lattice constant was 39.4nm. Besides the main peak, the formation of other miscellaneous peaks was analyzed and obtained by jade software. There are obvious miscellaneous peaks at 27.64°, 45.1° and 55.98°, and the comparison shows that the miscellaneous peaks are basically consistent with the standard peaks of SrMoO_4 . The XRD results are shown in Figure 2, where SrMoO_4 is marked with blue heart, which may be caused by the fact that when calcining SFM powder, it is in an air atmosphere. To eliminate miscellaneous peaks, calcination in a hydrogen atmosphere can be considered. The double perovskite structure of SFM can be more accurately described as a twisted cubic perovskite, in which Sr is +2 valence, Fe +4 valence and Mo +6 valence. There are also some Fe^{3+} and Mo^{5+} electron pairs. Although there are fewer oxygen vacancy in SFM, the p orbital of Fe and the d orbital of O are strongly hybridized, which facilitates the transmission of electrons and oxygen ions. This also allows SFM to show high catalytic reforming performance in low concentration gas fuels.

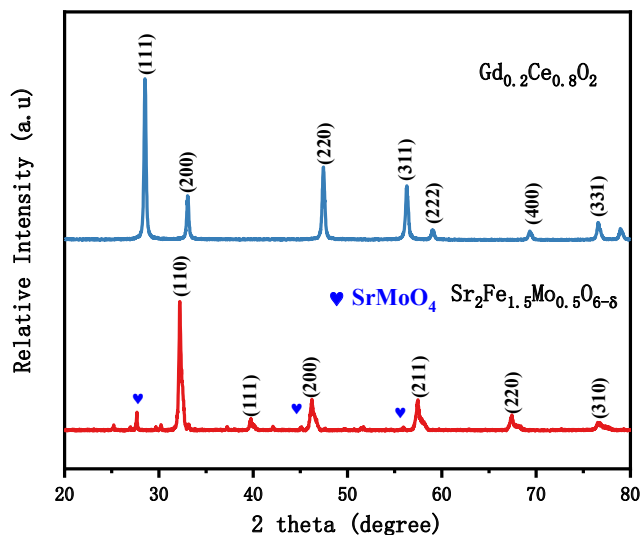


Fig.1 XRD patterns of SFM and GDC

4 Electrochemical performance analysis of the whole cell

First of all, will be completed the preparation of NiO - YSZ | YSZ | GDC | LSCF GDC and SFM GDC | NiO - YSZ | YSZ | GDC | LSCF - GDC both single battery test, SFM - GDC reforming layer have been analyzed the effect of battery for low concentration gas fuel, The electrochemical impedance of the I-V-P and EIS of the

two batteries were tested respectively in the H2 atmosphere of (3% H_2O) for comparative study. After the H2 atmosphere was tested, the gas was changed into a low-concentration gas simulation atmosphere. The atmosphere is composed of CH_4 of 8sccm and N_2 of 22.9sccm, and the ratio of CH_4 to O_2 is 2:1, which satisfies the coefficient relation of the chemical equation of oxidation reforming of CH_4 .

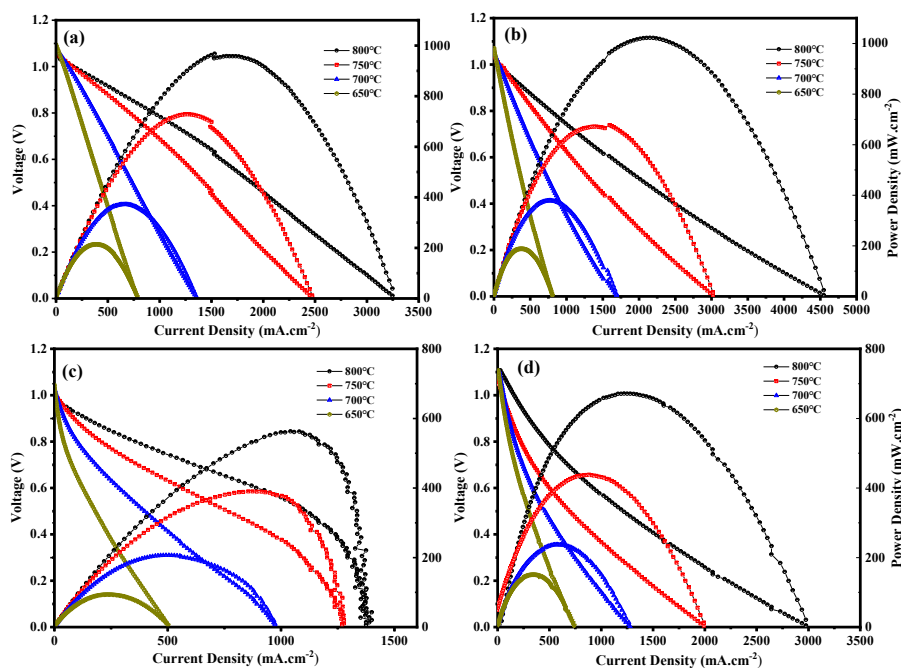


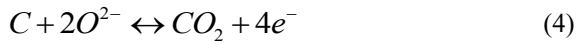
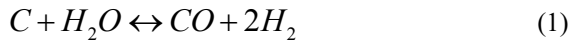
Fig.2 (a)I-V-P of ordinary straight-hole cell under H₂ atmosphere; (b)I-V-P of straight-hole cell with SFM-GDC reforming layer added under H₂ atmosphere; (c)I-V-P of ordinary straight-hole cell under LC-CMG atmosphere; (d)I-V-P of the straight-pore cell with SFM-GDC reforming layer added under LC-CMG atmosphere

The cathode of the ordinary straight-hole battery and the two kinds of battery with SFM reforming layer was exposed to air, and the anode passed wet H₂ as fuel to test the I-V-P performance. The electrochemical performance was tested every 50°C after the temperature was lowered from 800°C to 650°C. The open-circuit voltage of the ordinary straight-hole battery and the two kinds of battery with SFM reforming layer was tested at 800°C. They are 1.01V and 1.0409V respectively, indicating that YSZ electrolyte sintering has reached densification. The actual test open-circuit voltage value is slightly lower than the theoretical calculation of the open-circuit voltage, because the seal can not get the absolute ideal state. With the decrease of temperature, the open-circuit voltage increases. The open-circuit voltage of the battery with and without reforming layer from 800°C to 650°C is 1.0409, 1.056, 1.081, 1.0951V and 1.01, 1.04, 1.06, 1.07V, respectively. The battery with SFM reforming layer is slightly lower than that of the ordinary straight-hole battery. The I-V curves of the two cells in H₂ atmosphere basically conform to the linear relationship, which indicates that the interface polarization loss of the battery is small, and the open-circuit voltage loss is mainly due to the ohmic impedance of the electrolyte. As shown in FIG. 4(a) and (b), the I-V-P results of the two kinds of batteries under H₂ atmosphere show that the peak power density at 800°C is 950.02mW.cm⁻² and 1022.02mW.cm⁻², respectively. The maximum power densities from 800°C to 650°C are 950.02, 728.38, 372.24, 215.76 mW.cm⁻² and 1022.02, 671.09, 378.83, 190.54 mW.cm⁻², respectively. After adding SFM reforming layer to the anode of the conventional straight-hole battery, the maximum peak power density at 800°C increases to a certain extent in the hydrogen atmosphere, and at other temperatures, both are higher or lower, but within the range of plus or minus

50, indicating that the addition of SFM-GDC reforming layer will not have adverse effects on the electrochemical power performance of the hydrogen fuel straight-hole battery. It does not hinder the diffusion of hydrogen through the anode.

When low concentration gas fuel is used, methane pyrolysis in the anode, CH₄ is first adsorbed on the surface of Ni metal. In high temperature atmosphere, methane is catalyzed by Ni metal to break the C-H bond, generating carbon attached to the surface of Ni metal, and diffused in other parts of Ni metal. Carbon accumulates continuously on the surface of Ni metal, forming carbon whisker and growing continuously. Finally, the whole Ni metal is wrapped, so that it eventually loses its catalytic ability completely, and the battery power density drops to zero [18,19]. The selected simulated low-concentration gas atmosphere is that the ratio of methane to oxygen is 2:1, which conforms to the chemical equation of partial oxidative reforming of methane, as shown in Equation 1 [20]. Most methane is reformed to produce CO and H₂, and the cathode has a catalytic effect. Under the action of concentration gradient, the generated O²⁻ is transported to the interface between electrolyte and anode to react with syngas. The product of syngas is H₂O and CO₂, two oxidants which are conducive to the removal of anodic carbon deposit, as shown in Equations 1 and 2 [20]. At the same time, a layer of SFM-GDC reforming layer added to the anode of the straight hole battery transferred most of the methane cracking site to the outside of the anode. The compound of GDC also provides more three-phase reaction points for the reforming layer. SFM-GDC has excellent catalytic performance for partial oxidation reforming of methane, which can significantly improve the electrochemical reaction rate of the anode. This will also bring more O²⁻ to the anode. As an oxidizer, oxygen

ions can react with carbon deposits while reacting with fuel, and timely remove carbon deposits. The reaction equation is shown in Equations 3 and 4.



Based on the above reactions, straight hole Ni-based SOFC with SSFM-GDC reforming layer has excellent electrochemical power density and long-term stability when using low concentration gas fuel.

5 Analysis of long-term stability of SOFC and section morphology

5.1 Long-term stability analysis

The low-concentration gas atmosphere with methane oxygen ratio of 2:1 was used for a total of five days of testing. After the battery test, the long-term discharge stability test was carried out. After the stability test, the cross-section of the battery was characterized by scanning electron microscopy. Voltage output has been stable, no obvious fluctuation and attenuation, voltage remains near 0.8V, voltage attenuation rate is only 0.0004V/h, the battery has not been damaged, considering that the battery has been tested for several days before the long-term discharge test battery electrochemical test and tail gas chromatography test, still has very excellent stability performance. This not only shows that solid oxide fuel cells have good adaptability to low-concentration gas fuel gases, and can use low-concentration gas for fuel cells to generate electricity, but also shows that the SSFM-GDC reforming layer has excellent reforming catalytic effect and carbon resistance, and can maintain a stable working state. Figure 3 shows the constant-current test results of the battery under low-concentration gas atmosphere.

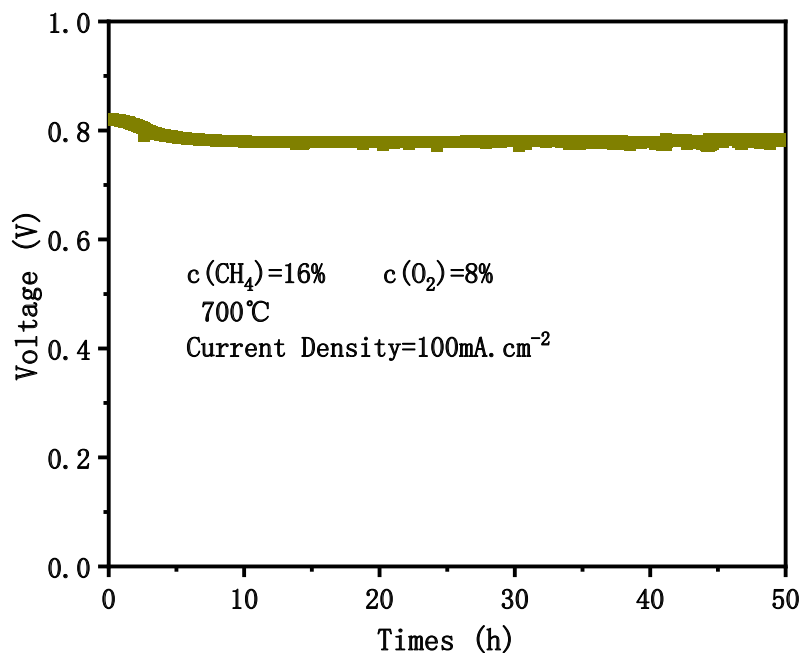


Fig.3 Long-term stability discharge test

5.2 Analysis of the morphology of the reforming layer cell

The test results of the microstructure morphology of the battery with SFM reforming layer after long-term testing in a low-concentration gas atmosphere are shown in FIG. 12. FIG. (a) is the scanning electron microscope image of the battery section after long-term testing. The electrolyte thickness of 12 ensures that the ohmic impedance of the battery is not too large, reduces the polarization loss of the battery in the electrolyte part, and ensures a high output power density of the battery. Figure (b) shows the test results of the anode support body of the battery. It

can be seen that the anode of the battery has a regular through-hole structure, which is conducive to reducing the transmission distance of fuel gas, reducing the concentration polarization, and improving the battery power density. Figure (c) shows the EDS spectrum test results of the anode section of the battery. It can be seen that after long-term test, there is still some carbon deposition in the anode of the battery, but the presence of SFM reforming layer transfers most of the methane cracking to the outside of the anode, and also provides catalytic reforming of methane, which significantly improves the electrochemical performance of the cell.

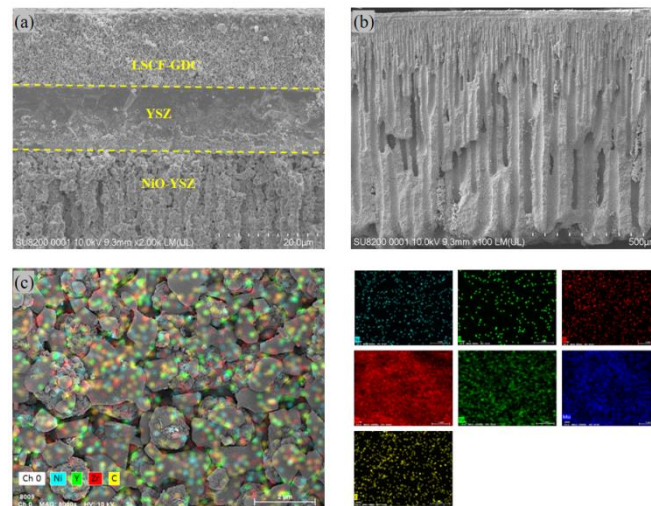


Fig.4 (a)SEM of the cross-section of the cell after testing; (b)SEM of the cross-section of the anode support; (c)and EDS of the cross-section of the anode

6 Conclusion

In this paper, the electrochemical performance of straight cell coated with SSFM-GDC reforming layer has been studied. Low concentration gas in coal mine contains methane, oxygen, nitrogen, and water hydrogen sulfide, etc., and its reaction process in solid oxide fuel cells is complicated. Therefore, studying the reaction mechanism of low concentration gas in solid oxide fuel cells has important practical significance for promoting its application.

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