SPECIAL ISSUE - RESEARCH ARTICLE

Enhanced coking resistance of Ni cermet anodes for solid oxide fuel cells based on methane on-cell reforming by a redox-stable double-perovskite $Sr_2MoFeO_{6-\delta}$

Hong Chang¹ | Huili Chen¹ | Guangming Yang² | Jing Shi³ | Wei Zhou² | Jianping Bai⁴ | Yuekui Wang¹ | Si-Dian Li¹

¹Institute of Molecular Science, Key Lab Mat Energy Convers and Storage Shanxi Province, Shanxi University, Taiyuan 030006, China

²State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, No. 5 Xin Mofan Road, Nanjing 210009, China

³Analytical Instrumentation center, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan 030001, China

⁴ State Key Laboratory of Coal and CBG Coming, Shanxi Lanyan Coalbed Methane, Group Co. Ltd, Jincheng 048204, China

Correspondence

Huili Chen, Institute of Molecular Science, Key Lab Mat Energy Convers and Storage Shanxi Province, Shanxi University, Taiyuan 030006, China. Email: huilichen@sxu.edu.cn

Funding information

Open Funding from State Key Laboratory of Material-oriented Chemical Engineering, Grant/Award Number: KL16-03; Shanxi Scholarship Council of China, Grant/Award Number: 2016-010; Shanxi Province Science Foundation, Grant/ Award Number: 2016011025; Coal Seam Gas Joint Foundation of Shanxi, Grant/ Award Number: 2015012016; Shanxi "1331 Project" Key Innovative Research Team, Grant/Award Number: "1331KIRT"

Summary

Carbon deposition on a Ni-based anode is troublesome for the direct power generation from methane-based fuels using solid oxide fuel cell. In this paper, a redox-stable double-perovskite $Sr_2MoFeO_{6-\delta}$ (SMFO) is applied as an independent on-cell reforming catalyst over a Ni-YSZ anode to improve coking resistance. The morphology, catalytic activity and electrochemical performance for wet methane/coal-bed gas (CBG) are investigated. A Ni-YSZ anode supported cell with SMFO generates a high power output of 1.77 W·cm⁻² and exhibits favorable stability operated on wet CH₄ at 800°C. Post-mortem micro-structural analyses of cells indicate the cell operated on CBG shows coking probably due to the heavy carbon compounds in CBG.

KEYWORDS

coking resistance, independent catalyst layer, methane fuels, solid oxide fuel cell

1 | INTRODUCTION

Solid oxide fuel cell (SOFC) is a promising power generation device with high energy efficiency and low environmental pollution. It could directly convert chemical energy in fuel to electricity via electrochemical reaction between fuel and oxygen. The superiority of SOFC over other fuel cells is fuel flexibility. Theoretically, all

DOI: 10.1002/er.4106

-WILEY- ENERGY RESEARCH

reductive fuels can be directly used as SOFC fuels, such as H_2 , carbonaceous species, H_2S^1 or $NH_3^{2,3}$ etc, which are oxidized by oxygen anion transferring from electrolyte. When H₂ is fed, Ni-based cermets are commonly used as SOFC anode materials and have shown excellent performance because of its desirable catalytic activity towards H₂ electrochemical oxidation, good chemical and mechanical stability, low cost and so on. However, when hydrocarbon fuels are used, there are some practical troubles such as carbon deposition on the Ni-YSZ anode because Ni exhibits an excellent catalytic ability for C—H cracking, which is detrimental to cell stability of SOFC. Therefore, in practical application, an additional reforming/oxidation procedure for the hydrocarbon fuels is needed before they are introduced into the anode of the SOFC. Under this circumstance, system complexity is increased with additional cost and low energy efficiency. A more economical and efficient way is direct utilization of those hydrocarbon fuels without extra pretreatment. For this purpose, the first step is to improve the anode of SOFC which is not only catalytically active for breaking the C—H bond with subsequent release of syngas, but also be electron conductive. In recent years, oxygen-deficient and mixed-valent perovskite materials⁴⁻⁸ have been shown to have a potential application as SOFC anode materials because of their appropriate catalytic activity and electro-conductivity. For example, molybdenum-based double perovskites $Sr_2MMoO_{6-\delta}$ (M = Co, Ni, Fe, Mn, and Mg) have exhibited excellent catalytic activity towards the electrooxidation of H_2 and CH_4 .⁹⁻¹² Among these oxides, Sr₂NiMoO_{6-δ} shows desirable electrochemical performance even in dry CH₄, which is attributed to the increased catalytic activity for methane conversion because of in situ exsolution of Ni.¹³ As a result, stability of catalyst decreases at low oxygen partial pressures. For most of perovskite materials, the electron-conductivity and catalytic activity are insufficient compared to the state-of-art Ni cermet anode materials. Anyway, Ni-based cermet remains the material of best choice for a SOFC anode. Nevertheless, the Ni cermet anode needs to be optimized to improve coking resistance. Therefore, substantial efforts have been attempted, such as metal alloying,¹⁴⁻¹⁶ changing ionic conductor phase,^{17,18} or modifying to the Ni-based anode surface or the bulk.¹⁹⁻ ²² As we know, coking is caused due to the pyrolysis of hydrocarbon on Ni surface. Preventing direct contact between hydrocarbon and Ni particles would decrease coking. For this purpose, an extra catalyst layer for hydrocarbon conversion between the Ni-based anode and hydrocarbon fuels seems to be an effective way. In this case, most of hydrocarbon fuels are catalytically reformed/oxidized into syngas before they meet the Nibased anode. In our recent paper,²³ we reported a new strategy to increase coking resistance of a Ni-based anode by applying an independent $La_{0.8}Sr_{0.2}Co_{0.4}Fe_{0.6}O_3(LSCF)$ anode catalyst layer. Unfortunately, LSCF is unstable at low oxygen partial pressures and is reduced to a K₂NiF₄-type oxide (Sr,La)FeO₄ with well-dispersed CoFe alloy nanoparticles. A decreased stability is predicted because of the segregation of the metal after a long time. Chuang also reported that coating LSCF catalyst layer on the anode surface of Ni-YSZ just delayed fuel cell cracking and carbon deposition on Ni particles still was found with C/Ni weight ratio of 0.1 after exposure to methane for 475 hours.²⁴

In this work, a redox-stable double-perovskite Sr₂MoFeO_{6-δ} (SMFO) is applied as an independent oncell reforming catalyst with the aim of improving coking resistance of a Ni-YSZ anode. A Ni-YSZ anodesupported cell with an independent SMFO catalyst layer was fabricated and evaluated for power generation fed with CH₄-based fuels. Aging test in galvano-static mode when feeding the cell with 3% humidified CH₄ and coalbed gas (CBG) are performed. The results indicate that the SMFO-modified cells show excellent operational stability, as well as high coking-resistant ability compared with the cell without the catalyst layer. For wet methane fuel, the voltage in galvano-static mode shows an initial increment, then a stable discharge profile over 55 hours without obvious decay is observed. For the wet CBG fuel, the cell voltage shows a slow and gradual decay. While for the cell without the catalyst layer, the cell performance shows a rapid decay with the voltage dropping to zero after exposure to CH₄-based fuels for only 20 minutes under the similar discharge condition. Besides, applying the SMFO catalyst layer in another cell with the structure of NiO-YSZ/YSZ/SDC/BSCF-SDC, the SMFO-modified cell exhibits excellent outperforms of 1.77 W⋅cm⁻² under wet CH₄ operation at 800°C.

2 | EXPERIMENTAL SECTION

2.1 | Materials and powder preparation

Nano-scale NiO powder and YSZ powder were purchased from the Chengdu Shudu Nano-materials Technology Development Co., Ltd (Sichuan, China) and Shandong Jinao Technology Advanced Materials Co., Ltd, respectively. Cathode $La_{0.8}Sr_{0.2}MnO_{3-\delta}(LSM)$ powder was provided by the Ningbo Institute of Industrial Technology. Bottled gases are applied to the anode of SOFC. CBG is provided by a local commercial gas station (composition: CH₄, 82.9975%; O₂, 2.1853%; N₂,10.1839%; C₂-C₈,3.4731%; CO₂,1.1602%). Electrolyte powder Sm_{0.2}Ce_{0.8}O_{1.9}(SDC) is prepared by hydrothermal synthesis as reported.²⁵ Cathode powder Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃(BSCF) and catalyst material SMFO were prepared via the EDTA-CA sol-gel method. The preparation of SMFO is taken as an example: first dissolving the appropriate amount of $Fe(NO_3)_3$, $Sr(NO_3)_2$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $NH_3\cdot H_2O$, and EDTA as well as citric acid (CA) into deionized water according to the mole ratio of EDTA: CA: M^{n+} : $NH_3\cdot H_2O$ was 1:2:1:10. The solution was churned acutely and heated until the yellow gel formed. Then, the SMFO precursor was obtained via the calcination at 1100°C for 2 hours in a muffle furnace to remove the organic impurities. The desired perovskite SMFO was obtained after treated at 900°C in dry H_2 for 2 hours.

2.2 | Catalyst layer and cell fabrication

To increase the mechanical properties of the catalyst layer, a double-layered slice SMFO-Al₂O₃ was prepared by a dual dry-pressing/sintering method as followings: first, 0.25-g powder of Al₂O₃ and PVB in a weight ratio of 25:3 was pressed to form a substrate disk using a given steel mold (Φ 13 mm) under a pressure of 145 MPa; then, 0.035-g powder of SMFO and PVB in a weight ratio of 7:3 was homogenously distributed over the substrate surface and co-pressed under a pressure of 230 MPa. A double-layered slice was obtained and was further calcined at 900°C for 4 hours.

Two kinds of anode-supported cells, with the structure of NiO-YSZ/YSZ/LSM-YSZ (named as CP (Ni-YSZ) ~LSM) and NiO-YSZ/YSZ/SDC/BSCF-SDC (named as TP (Ni-YSZ)~BSCF) were used in this work. For CP (Ni-YSZ)~LSM, the half-cell (the weight ratio of NiO/YSZ is 6:4) with a YSZ electrolyte layer was fabricated by a dual dry-pressing in a stainless steel mold (ϕ 13 mm) and cosintering for 5 hours at 1400°C. Then, the LSM-YSZ (the weight ratio of LSM/YSZ is 7:3) slurry dispersed in isopropyl alcohol was spray-painted on the electrolyte disc and was sintered for 2 hours at 1100°C. Cells with and without SMFO catalyst are designated as "SMFO// NiO-YSZ" and "NiO-YSZ", respectively. For TP (Ni-YSZ) ~BSCF, the anode layer was prepared using a tape-casting approach; then, the electrolyte layer and the cathode layer were sprayed in sequence. The thin SDC buffer layer is used to prevent side-reaction between YSZ and BSCF. The detailed procedures were available in our reported paper.²⁶

Diluted silver paste was coated on the cathode surface as the current collectors. Silver wires were stuck to the anode surface and the cathode surface, respectively, to conduct current. The double-layered catalyst slice and the button cell were sealed onto a quartz tube, in which the anode surface of cell is towards the catalyst layer.

WILEY ENERGY R 2.3 | Basic characterization

The crystallgraphic information of the catalyst powder was analyzed by X-ray diffraction (XRD) with Cu $K\alpha$ radiation, scanning in the range of 20°-80° at room temperature. The morphologies of cell were identified using A JSM6700 JEOL scanning electron microscopy (SEM), and the elemental information was collected from the Bruker energy dispersive X-ray (EDX) spectrometer.

ENERGY RESEARCH

 N_2 absorption/desorption isothermal experiments were conducted using a Micromeritics ASAP-2020 M automated analyzer (USA). The electrochemical performances were recorded by an Iviumstat electrochemical workstation from 750°C to 850°C with a 50°C interval using 4-wire and the 2 electrodes setup. H_2 or humidified CH₄ or CBG as fuel was fed at a flow rate of 80 mL min⁻¹. Surrounding air acted as the oxidant. Prior to the test, cells were in situ reduced in pure H_2 at 700°C for 1 hour. The electrochemical impedance spectra (EIS) were recorded at open circuit voltage with an alternate current signal amplitude of 10 mV in a frequency range from 10^5 Hz to 0.1 Hz.

2.4 | Catalytic activity test

The catalytic performance of the in situ-reduced SMFO for methane steam reforming (MSR) and methane partial oxidation (MPO) was evaluated on a fixed-bed reactor. First, 200-mg catalyst particles (40-60 mesh) mixed with 400-mg quartz sands were loaded into the reactor. Then, the gas mixture (V_{CH4} : V_{H2O} = 2:1, or V_{CH4} : V_{O2} = 2:1) was fed into the reactor, in which a CH₄ flow rate of 10 mL min⁻¹ was controlled. A microsyringe pump was used to pump water into the tube wrapped with heating jacket. The effluent gases were fed into gas chromatograph (Agilent 7820) for on-line analysis with a helium carrier flow rate of 80 mL min⁻¹. Poraplot Q/Hayesep Q/5 Å sieve molecular column was used to detect and separate CO, CO₂, and CH₄. The test was carried out for MPO from 400°C to 950°C and MSR from 750°C to 900°C, respectively. CO selectivity and CH₄ conversion were used to evaluate the catalytic activity of the sample, and the detailed calculation method was available in our reported paper.²⁷

3 | **RESULTS AND DISCUSSION**

3.1 | XRD patterns of SMFO

For the SMFO precursor calcined under an air atmosphere, a mixed lattice phase of double perovskite SMFO [JCPDS 70-4088] with $SrMoO_4$ [JCPDS 08-0482] is observed (Figure 1A), which is in agreement with



FIGURE 1 XRD patterns of A, the SMFO precursor calcined under an air atmosphere and B, SMFO calcinations at 900°C in a reducing atmosphere

reference.²⁸ The mass fraction of SMFO and SrMoO₄, obtained by Rietveld refinement of the XRD patterns (Figure S1), is 69.0% and 31.0%, respectively. The space group of SMFO and SrMoO₄, is I4/mmm and I41/a, respectively. The lattice parameters of SMFO and SrMoO₄, are observed to be a = b = 5.5643 (2) Å, c = 7.8888 (5) Å and a = b = 5.3921 (2) Å, c = 12.0597 (6) Å (Rwp = 6.96%, Rp = 25.49%, CHI^2 = 1.344), respectively. In the SMFO phase, the molar ratio of Sr: Mo:Fe is 2:0.7464:1.2536. After reduction in a reducing atmosphere for 2 hours at 800°C, most of SrMoO₄ disappears, and more double-perovskite SMFO forms (88.9 wt.%) (Figure 1B). The I4/mmm space group of SMFO is retained with a = b = 5.5700 (3) and

c = 7.9029 (7) (Rwp = 10.70%, Rp = 7.75%, CHI^2 = 12.36). While the molar ratio of Sr:Mo:Fe in the SMFO phase is changed to 2:0.9436:1.0564. It indicates SMFO structure is stable under a H_2 atmosphere.

3.2 | Characteristic of the catalystmodified cell

An illustration of the cell assembly with a SMFO independent catalyst layer, and the cross-sectional microstructures of cell and catalysts layer are shown in Figure 2. A densified electrolyte layer with a thickness of 37-µm was observed. Simultaneously, both anode and cathode layer show high porosity, and keep in compact touching with electrolyte layer, which ensures a low contact resistance. Catalyst layer is constructed by 1.3-mm substrate and 60-µm catalyst.

In this SOFC assembly, fuels have to go through the catalyst layer before they reach to cell. Therefore, a large number of pores are necessary in the double-layered catalyst slice. Simultaneously, to improve the conversion efficiency of fuels, both a small pore size and large specific surface area are also essential. Herein, the pore parameters and specific surface area of the SMFO-Al₂O₃ catalyst slice were measured using N₂ physical adsorption. The BJH pore volume and the BET specific surface area are 0.2 cm³·g⁻¹ and 73.4 m²·g⁻¹, respectively. A type-H3 hysteresis loop is observed on the N₂ adsorption/desorption isotherm (Figure 3), indicating a mesoporous structure with slit-shaped nano-pores. An average pore size of ca. 9 nm is observed from the steep and sharp peak on the pore size distribution curve.



FIGURE 2 A, Illustration of the fuel cell test setup; B, the cross-sectional microstructures of cell and catalysts layer [Colour figure can be viewed at wileyonlinelibrary.com]



FIGURE 3 Nitrogen gas adsorption/desorption isotherm of the SMFO-Al₂O₃ catalyst layer. The inset is the pore size distribution of the sample [Colour figure can be viewed at wileyonlinelibrary. com]

3.3 | Catalytic activity evaluation for MPO and MSR

Coking resistance of a Ni-based anode is strongly associated with the catalytic performance of the catalyst layer towards CH_4 conversion. Under SOFC conditions, probably MPO and steam reforming (MSR) co-exist. Herein, the catalytic effectiveness of the in situ-reduced SMFO towards MPO and MSR at different temperatures was tested. As shown in Figure 4, for MPO, it is observed that the reaction starts initially at 400°C. Both CH_4 conversion and CO selectivity increase with temperature from 400°C to 900°C. The main product is CO_2 below 750°C. With the increment of temperature from 750°C to 900°C, the CH_4 conversion rises clearly from 26.3% to 36.4% accompanied by the increased CO selectivity from 17.6% and 55.5%.



FIGURE 4 Catalytic activity of the SMFO catalyst for MSR $(V_{H2O}:V_{CH4} = 1:1)$ and MPO $(V_{CH4}: V_{O2} = 2:1)$ [Colour figure can be viewed at wileyonlinelibrary.com]

While for MSR, it is noticeable that the reaction starts from 750°C and increases with temperature. When temperature elevates to 800°C, CO selectivity of 81.5% is achieved with CH₄ conversion of 19.2%. At 900°C, CH₄ conversion reaches 36.6% with CO selectivity of 97.2%. Compared with MSR, MPO shows lower CO selectivity, indicating partial CH₄ is deep oxidized into CO₂, which is unbeneficial for SOFC utilization.

ENERGY RESEARC

WILEY

3.4 | The electrochemical performance when feeding cell with wet CH_4 and wet CBG

It is desired that a Ni cermet anode with an independent SMFO catalyst layer would display a moderate coking resistance when using wet methane-based fuels due to the partial conversion of fuels. Vapor which is required in reforming reaction is provided by the bubbling water and the product from the electrochemical oxidation of H_2 . What is more, the catalyst layer can act as a diffusion barrier layer. As a result, some unconverted fuels would be exhausted along with the off gas. Thus, methane concentration near anode surface would greatly decrease.

In order to achieve good re-productivity, an anodesupported cell with high stability (NiO-YSZ/YSZ/LSM-YSZ), is used. Figure 5 shows the temperature-dependent electrochemical performances [I-V(P)] of the cells without (Figure 5A,C) and with (Figure 5B,D) the SMFO catalyst layer from 750°C to 850°C fed with wet CH₄ and wet CBG, respectively. Under wet CH₄ fuel operation, the blank cell without the catalyst layer [(Ni-YSZ)-CH₄] delivers peak power densities (PPDs) of 0.20, 0.34, and 0.55 W·cm⁻² at 750°C, 800°C, and 850°C, respectively (Figure 5A). While, the SMFOmodified cell [(SMFO//Ni-YSZ)-CH₄], shows PPDs of 0.24, 0.42, and 0.67 W·cm⁻² (Figure 5B) at the corresponding temperature, respectively. A 22% performance increment is achieved at 850°C for the SMFO-modified cell compared with the blank cell. With temperature decreasing, [(SMFO//Ni-YSZ)-CH₄] shows a similar performance to [(Ni-YSZ)-CH₄]. For instance, at 750° C, PPDs of [(SMFO//Ni-YSZ)-CH₄] and [(Ni-YSZ)-CH₄] are 0.24 and 0.20 W·cm⁻², respectively. Probably, it is attributed to the lower catalytic performance of the SMFO catalyst for MPO and MSR at the lower temperature. Under wet CBG operation, the performances of the cells without and with the catalyst layer were also obtained in a similar way (Figure 5C,D). The variation trend of performance with temperature is similar to that of the cells operated on CH4 fuel. PPD of [(SMFO//Ni-YSZ)-CBG] is 0.61 W·cm⁻², which is higher than 0.55 W·cm⁻² measured on [(Ni-YSZ)-CBG] at 850°C. A 9% performance increment is achieved. [(SMFO//Ni-



FIGURE 5 The I–V (P) curves for the cells without (A and C), and with the SMFO catalyst layer (B and D), fed with wet CH_4 and wet CBG at various temperature [Colour figure can be viewed at wileyonlinelibrary.com]

YSZ)-CH₄] exhibits higher performance than [(SMFO// Ni-YSZ)-CBG]. For example, PPD of [(SMFO//Ni-YSZ)-CH₄] is 0.67 W·cm⁻² with a maximum current density (MCD) of ~2558 mA·cm⁻². While, [(SMFO//Ni-YSZ)-CBG] delivers a PPD of 0.61 W·cm⁻² with a MCD of ~2250 mA·cm⁻². Probably, heavy carbon compounds in CBG have a negative effect on cell performance, which is in agreement with the previous work.²³

Generally, the resistances are deconvoluted roughly into 2 sections: the polarization resistance (R_P) and the ohmic resistance (R_o). By and large, R_o primarily stems from the electronic resistance from electrodes, the ionic resistance from electrolytes, the resistance from wires of the exterior circuit, and the resistance from the electrodeelectrolyte interfaces. For a well-fabricated cell, the value of R_o approximately equals to the ionic resistance from electrolytes due to the good electronic conductivity of electrode, which is constant and not affected by the polarization process.^{29,30} Therefore, R_o will not be discussed further. R_P consists of the electrode polarization resistance related to the low-frequency arc (R_L , 10^0 - 10^2 Hz) and the high-frequency arc (R_H , 10^2 - 10^5 Hz). It is generally accepted that R_H is strongly influenced by the chargetransfer process (associated with the electrode reaction), and R_L is dependent on the mass-transfer process (the process of the gas-phase diffusion and dissociative adsorption).²⁹ Figure 6A,B presents the Nyquist plot and Bode plot of EIS for the cells without and with the



FIGURE 6 Comparison of the Nyquist plot A, and bode plot B, of EIS for the cells with and without the SMFO catalyst layer at 850°C under CH₄ operation, respectively [Colour figure can be viewed at wileyonlinelibrary.com]

SMFO-Al₂O₃ layer fed with wet CH₄ at 850°C, respectively. In Figure 6A, [(SMFO//Ni-YSZ)-CH₄] shows a smaller R_p than [(Ni-YSZ)-CH₄], especially R_L , which indicates a smaller mass transfer resistance. In Figure 6B, [(SMFO// Ni-YSZ)-CH₄] shows lower impedance in the whole frequency domain than [(Ni-YSZ)-CH₄], indicating that both the charge transfer and fuel diffusion are sped up after the application of catalyst layer. Bode plot of [(Ni-YSZ)-CH₄] shows 2 summits at approximately 4 Hz and at 100 Hz in the whole frequency. While the Bode plot of [(SMFO// Ni-YSZ)-CH₄] shows only 1 summit at 37 Hz, indicating the application of catalyst speeds up the surface diffusion of fuels within the anode pores. These results further prove the conversion of methane fuel into small molecules H₂ and CO, which diffuse more easily than CH₄ molecules.

Figure 7A,B compares the electrochemical performance for the cells without and with the SMFO catalyst layer at 850°C when fed with wet CH_4 (A)/CBG (B), respectively. In a whole, the application of SMFO catalyst layer improves the cell performance. Especially, a less voltage loss at low current density is observed for the 2 SMFO-modified cells, indicating a lower anode polarization compared with the blank cells.

The performance of the SFMO-modified cell is further investigated using another kind of cell with the configuration of SMFO//TP (Ni-YSZ)~BSCF. The cell achieved a PPD of 1.77 W·cm⁻² at 800°C (Figure 8), which is much higher than that of before-mentioned cell with the structure of SMFO//CP (Ni-YSZ)~LSM.

3.5 | Aging tests in galvano-static mode when feeding the cell with wet CH_4 and wet CBG

The operation stability over time is an important aspect for the practical application of SOFC. Figure 9 shows the discharge profiles of the cells without and with the SMFO-Al₂O₃ layer when fed with wet CH₄/CBG at 800°C, respectively. The voltage of cells is monitored in



FIGURE 8 Comparison of the electrochemical performance of SMFO//TP (Ni-YSZ)~BSCF and SMFO//CP (Ni-YSZ)~LSM under CH₄ operation at 800°C [Colour figure can be viewed at wileyonlinelibrary.com]



FIGURE 9 Aging tests in galvanostatic mode for the cells with and without the SMFO catalyst layer when feeding the cell with wet CH₄ and wet CBG at 800°C, respectively [Colour figure can be viewed at wileyonlinelibrary.com]



FIGURE 7 Comparison of I-V(P) curves for the cells with and without the SMFO catalyst layer fueled with A, wet CH₄ and B, wet CBG at 850°C, respectively [Colour figure can be viewed at wileyonlinelibrary.com]

WILEY ENERGY RESEARCH

galvano-static mode with current density of 333 mA·cm $^{-2}$. It is observed that the cell voltage without the catalyst layer instantly drops to zero after exposure to fuels for approximately 20 minutes. While, under CH₄ operation, the SMFO-modified cell delivers superior stability over at least 55 hours. Interestingly, the voltage increases in the initial 15 hours and holds at the value of 0.7 V in the following period. Probably, at the beginning when wet CH₄ is fed, because of the insufficient steam and lattice oxygen on catalyst, soon carbon deposition on the Ni-based anode occurs, which leads to a cell voltage drop. With the proceeding of SOFC running, more oxygen ions transfer to anode through electrolyte, and more H₂O are produced from the electro-oxidation

of H₂, which are favorable for removing the carbon deposits. The combined actions induce the carbon elimination speed is faster than the carbon deposition rate. Therefore, with carbon deposit removed, cell voltage increases after a short period. Nevertheless, under CBG operation, the SMFO-modified cell shows a gradual voltage drop with an average drop rate of 0.002 V·h⁻¹ within 55 hours. For CBG, carbon deposition comes from CH₄ and heavy hydrocarbon complexes. More carbon deposition speed is faster than the carbon elimination speed. The durability operated on wet CH₄ suggests that the SMFO-modified Ni-YSZ anode has a good coking resistance.



FIGURE 10 SEMs of A, freshly reduced anode surface of the cell; B, the anode surface of the blank cell without the catalyst layer after aging test in wet CH_4 for 20 minutes; C and D, the anode surface of the SMFO-modified cell with the catalyst layer after aging test in wet CH_4 for 55 hours and in wet CBG for 55 hours, respectively; E, the freshly reduced surface of the SMFO catalyst layer; F, the catalyst surface of the SMFO-modified cell after aging test in wet CH_4 for 55 hours

3.6 | Post-mortem microstructural analyses of cells

The microstructure of the catalyst layer and the anode layer were analyzed before and after aging test. Both the catalyst layer and the anode layer are porous before aging test (Figure 10A,E). After aging test, the anode layer of the cell without the catalyst layer exhibits a close-knit grain morphology without any clearance (Figure 10B). While, the anode layer of the SMFO-modified cells keeps integrated with the porous morphology (Figure 10C,D). What deserves to be mentioned that sintering to some extent occurs for the anode and SMFO of the SMFOmodified cell (Figure 10C,D,F) after aging tests operated on wet CH₄ and wet CBG, which is not beneficial to gas passing through. All of these results indicate that the thermal stability of SMFO and anode materials needs to be improved.

EDX analysis was also carried out for the SMFOmodified cells after aging test operated on wet $CH_4/$ CBG and the related mean-carbon-content (MCC) on the anode and catalyst surface are listed in Table 1. For the SMFO-modified cell, the MCC on the anode surface is around 19.6 at.% after aging test in wet CH_4 , which is close to the MCC of 22.4 at.% on a fresh anode surface. Similarly, the MCC on the corresponding catalyst surface is 13.1 at. % after aging test, which is slightly higher than the MCC of 10.2 at.% on a freshly reduced catalyst surface. For the SMFO-modified cell tested in wet CBG for 55 hours, the MCCs on the surface of the anode and catalyst are 49.5 at.% and 13.3 at.%, respectively, which are higher than those tested in wet CH_4 under the same condition.

Post-mortem micro-structural analyses of cells operating on methane-based fuels display that applying SMFO catalyst could obviously improve coking resistance of a Ni-YSZ anode. When operated on wet CBG, the anode surface of SMFO-modified cell shows much more coking than that on wet CH₄, indicating that impurities in CBG

TABLE 1 EDX analyses of the anode surface and catalyst surfaceof the SMFO-modified cells after aging tests in wet CH_4 and wetCBG

	Mean Carbon Content, at. %	
Surface	Anode surface	Catalyst surface
The freshly reduced surface	22.4	10.2
(SMFO//Ni-YSZ)-CH ₄ after aging test for 55 h	19.6	13.1
(SMFO//Ni-YSZ)-CBG after aging test for 55 h	49.5	13.3

such as the heavy carbon compounds is accelerating carbon deposition.

FNFRGY

3.7 | The catalytic mechanism of SMFO

WILEY

It is thought that the catalytic oxidation of methane on oxide agrees with the MVK mechanism,³¹ in which gaseous methane molecules are adsorbed and react with the surface lattice oxygen in oxide with the subsequent formation of surface oxygen vacancies, then the resulting oxide vacancies in oxide are rapidly refilled from the gaseous oxygen. Therefore, oxygen-baring species, such as steam, will be captured by oxygen vacancies. The rate-limiting step of methane oxidation is related to the oxygen species on the catalyst surface. Kinetics studies have suggested that both the adsorbed and lattice oxygen species have a contribution to the oxidation of methane when temperature is over 327°C. In addition, for catalytic oxidation of CH₄, an electron transfer happens from carbon to oxygen on the catalyst surface; therefore, the electrical conductivity of the material plays an important role in the whole oxidation process. SMFO was reported to have a half-metallic character, which endows it with a perfect candidate for heterogeneous catalytic processes. In fact, SMFO has been reported to have a high catalytic activity towards methane oxidation, which is attributed to its defective character. There is an abundance of inherent oxygen vacancies in SMFO due to the substitution of Mo by a low-valance metal ion. Under a reducing atmosphere, more oxygen vacancies are generated due to the change of metal oxidation state. Wang indicated the coexistence of Fe³⁺-Mo⁵⁺ and Fe²⁺-Mo⁶⁺ pairs in SMFO.³²

In our experiment, water-humidified CH_4 is, first, partially oxidized into H_2 and CO by the surface lattice oxygen atoms of the catalyst and the fueled steam. Then, H_2 is electrochemically oxidized to produce more H_2O in the anode. Next, the produced H_2O is activated by the SMFO catalyst and further oxidizes CH_4 to produce H_2 and CO.

4 | CONCLUSION

Double-layered SMFO– Al_2O_3 is applied as an independent catalyst layer to improve coking resistance of a Ni cermet anode of SOFC. The results indicate that the SMFO-modified cell shows improved performance and better stability compared with the blank cell without the catalyst layer when fueled with methane-based gas, which is attributed to the fuel reforming/oxidation from hydrocarbon to the coking insusceptible CO and H₂. However, because the SMFO catalyst has medium catalytic activity for methane conversion, coking on a

2536

WILEY ENERGY RESEARCH

Ni-based anode still occurs after a long operation period. The cell fueled with wet CBG shows a more serious coking than that for wet methane because of the negative effect from heavy carbon compounds in CBG. Besides, applying the SMFO catalyst layer in the tape-casting cell with the structure of NiO-YSZ/YSZ/ SDC/BSCF-SDC, the modified cell exhibits excellent outperforms of 1.77 W·cm⁻² operated on wet CH₄ at 800°C. The loading mode of the catalyst layer facilitates the detailed study on the anode surface because the catalyst layer and the anode are mutually independent. Obviously, the catalyst loading mode is not applicable for a planar SOFC stack because of the demand of close packing between the neighbor cells. Probably, it may be used in a tubular SOFC stack, in which the solid oxide tube functions as the anode or cathode, and other cell components are coated around the tube in layers. The porous catalyst layer can be internally or externally placed which neighbors the anode layer.

ACKNOWLEDGEMENT

This work was supported by the Coal Seam Gas Joint Foundation of Shanxi (2015012016); Shanxi Province Science Foundation (2016011025); Shanxi Scholarship Council of China (2016-010); Shanxi "1331 Project" Key Innovative Research Team ("1331KIRT"); and the Open Funding from State Key Laboratory of Material-oriented Chemical Engineering (No. KL16-03). The Scientific Instrument Center of Shanxi University is acknowledged for the SEM test.

ORCID

Huili Chen D http://orcid.org/0000-0002-1664-4121

REFERENCES

- 1. Monder DS, Vorontsov V, Luo JL, Chuang KT, Nandakumar K. An investigation of fuel composition and flow-rate effects in a H₂S fuelled sofc: experiments and thermodynamic analysis. *Can J Chem Eng.* 2012;90(4):1033-1042.
- Ni M, Leung MK, Leung DY. Ammonia-fed solid oxide fuel cells for power generation—a review. *Int J Energ Res.* 2009;33(11):943-959.
- 3. Meng G, Jiang C, Ma J, Ma Q, Liu X. Comparative study on the performance of a SDC-based SOFC fueled by ammonia and hydrogen. *J Power Sources*. 2007;173(1):189-193.
- Xu L, Yin YM, Zhou N, Wang ZW, Ma ZF. Sulfur tolerant redox stable layered perovskite SrLaFeO_{4-δ} as anode for solid oxide fuel cells. *Electrochem Commun.* 2017;76:51-54.
- Xu J, Zhou XL, Dong XL, Pan L, Sun KN. Catalytic activity of infiltrated La_{0.3}Sr_{0.7}Ti_{0.3}Fe_{0.7}O_{3-δ}-CeO₂ as a composite SOFC

anode material for H_2 and CO oxidation. Int J Hydrogen Energy. 2017;42(23):15632-15640.

- Tiwari PK, Yue XL, Irvine JTS, Basu S. La and Ca-doped A-site deficient strontium titanates anode for electrolyte supported direct methane solid oxide fuel cell. *J Electrochem Soc.* 2017;164(9):F1030-F1036.
- Sengodan S, Ju YW, Kwon O, et al. Self-decorated MnO nanoparticles on double perovskite solid oxide fuel cell anode by in situ exsolution. ACS Sustain Chem Eng. 2017;5(10):9207-9213.
- Kumar P, Presto S, Sinha ASK, Varma S, Viviani M, Singh P. Effect of samarium (Sm³⁺) doping on structure and electrical conductivity of double perovskite Sr₂NiMoO₆ as anode material for SOFC. *J Alloys Comp.* 2017;725:1123-1129.
- Zheng K, Swierczek K, Polfus JM, Sunding MF, Pishahang M, Norby T. Carbon deposition and sulfur poisoning in SrFe_{0.75}Mo_{0.25}O_{3-δ} and SrFe_{0.5}Mn_{0.25}Mo_{0.25}O_{3-δ} electrode materials for symmetrical SOFCs. *J Electrochem Soc.* 2015;162(9): F1078-F1087.
- 10. Xie ZX, Zhao HL, Du ZH, Chen T, Chen N. Electrical, chemical, and electrochemical properties of double perovskite oxides $Sr_2Mg_{1-x}Ni_xMoO_{6-\delta}$ as anode materials for solid oxide fuel cells. *J Phys Chem C*. 2014;118(33):18853-18860.
- Jiang L, Liang G, Han JT, Huang YH. Effects of Sr-site deficiency on structure and electrochemical performance in Sr₂MgMoO₆ for solid-oxide fuel cell. *J Power Sources*. 2014;270:441-448.
- Sasaki K, Shin-Mura K. Electrical conductivity of Sr₂MgMoO_{6-δ} for solid oxide fuel cell anodes. *J Cerma Soc Jpn.* 2017; 125(6):487-493.
- Huang Y-H, Liang G, Croft M, Lehtimaki M, Karppinen M, Goodenough JB. Double-perovskite anode materials Sr₂MMoO₆ (M= Co, Ni) for solid oxide fuel cells. *Chem Mater.* 2009; 21(11):2319-2326.
- Yoon Y, Kim H, Lee J. Enhanced catalytic behavior of Ni alloys in steam methane reforming. J Power Sources. 2017;359:450-457.
- 15. Pham HC, Taniguchi S, Inoue Y, et al. Modification of surface oxide layer of Fe-Cr-Al alloy with coating materials for SOFC applications. *Fuel Cells*. 2017;17(1):83-89.
- Li JC, Yu Y, Yin YM, Zhou N, Ma ZF. A novel high performance composite anode with in situ growth of Fe-Ni alloy nanoparticles for intermediate solid oxide fuel cells. *Electrochim Acta*. 2017;235:317-322.
- 17. Wang W, Chen YB, Wang F, Tade MO, Shao ZP. Enhanced electrochemical performance, water storage capability and coking resistance of a Ni+BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3- δ} anode for solid oxide fuel cells operating on ethanol. *Chem Eng Sci.* 2015;126:22-31.
- Wang W, Su C, Ran R, et al. Nickel-based anode with water storage capability to mitigate carbon deposition for direct ethanol solid oxide fuel cells. *ChemSusChem.* 2014;7(6):1719-1728.
- McIntyre MD, Kirtley JD, Singh A, Islam S, Hill JM, Walker RA. Comparing in situ carbon tolerances of Sn-infiltrated and BaOinfiltrated Ni-YSZ cermet anodes in solid oxide fuel cells exposed to methane. J Phys Chem C. 2015;119(14):7637-7647.

ILEY-FNFR

- 20. Huang B, Gu XZ, Hu YX, et al. Characterization of a Cu-La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃-CeO₂/La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃-YSZ/Ni-ScSZ three-layer structure anode in thin film solid oxide fuel cell running on methane fuel. *Fuel Cells*. 2015;15(2):398-407.
- Tao ZT, Hou GH, Xu N, Zhang QF. A highly coking-resistant solid oxide fuel cell with a nickel doped ceria: Ce_{1-x}Ni_xO_{2-y} reformation layer. *Int J Hydrogen Energy*. 2014;39(10):5113-5120.
- Wang F, Wang W, Ran R, Tade MO, Shao ZP. Aluminum oxide as a dual-functional modifier of Ni-based anodes of solid oxide fuel cells for operation on simulated biogas. *J Power Sources*. 2014;268:787-793.
- 23. Chang H, Chen HL, Shao ZP, Shi J, Bai JP, Li SD. In situ fabrication of (Sr, La) FeO₄ with CoFe alloy nanoparticles as an independent catalyst layer for direct methane-based solid oxide fuel cells with a nickel cermet anode. *J Mater Chem A*. 2016;4(36):13997-14007.
- 24. Mirzababaei J, Chuang SSC. La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ perovskite: a stable anode catalyst for direct methane solid oxide fuel cells. *Catalysts*. 2014;4(2):146-161.
- 25. Shi HG, Zhou W, Ran R, Shao ZP. Comparative study of doped ceria thin-film electrolytes prepared by wet powder spraying with powder synthesized via two techniques. *J Power Sources*. 2010;195(2):393-401.
- 26. Jiang SS, Sunarso J, Zhou W, Shao ZP. The significant effect of the phase composition on the oxygen reduction reaction activity of a layered oxide cathode. *J Mater Chem A*. 2013; 1(36):11026-11032.
- 27. Yang GM, Su C, Chen YB, Tade MO, Shao ZP. Nano La_{0.6}Ca_{0.4}Fe_{0.8}Ni_{0.2}O_{3-δ} decorated porous doped ceria as a novel cobalt-free electrode for "symmetrical" solid oxide fuel cells. *J Mater Chem A*. 2014;2(45):19526-19535.

- 28. Falcon H, Barbero JA, Araujo G, et al. Double perovskite oxides A_2 FeMoO_{6- δ}(A = Ca, Sr and Ba) as catalysts for methane combustion. *Appl Catal B-Environ*. 2004;53(1):37-45.
- 29. Lu ZG, Zhu JH, Bi ZH, Lu XC. A Co-Fe alloy as alternative anode for solid oxide fuel cell. *J Power Sources*. 2008;180(1): 172-175.
- 30. Guo T, Dong XL, Shirolkar MM, et al. Effects of cobalt addition on the catalytic activity of the Ni-YSZ anode functional layer and the electrochemical performance of solid oxide fuel cells. *ACS Appl Mater Interfaces*. 2014;6(18):16131-16139.
- Gür TM. Comprehensive review of methane conversion in solid oxide fuel cells: prospects for efficient electricity generation from natural gas. *Prog Energ Combust Sci.* 2016;54:1-64.
- Wang ZM, Tian Y, Li YD. Direct CH₄ fuel cell using Sr₂FeMoO₆ as an anode material. *J Power Sources*. 2011;196(15):6104-6109.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Chang H, Chen H, Yang G, et al. Enhanced coking resistance of Ni cermet anodes for solid oxide fuel cells based on methane on-cell reforming by a redox-stable double-perovskite $Sr_2MoFeO_{6-\delta}$. *Int J Energy Res.* 2019;43:2527–2537. https://doi.org/10.1002/er.4106