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Samaria-doped Ceria Modified Ni/YSZ Anode for Direct Methane Fuel in Tubular Solid Oxide Fuel Cells by Impregnation Method

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A porous NiO/yttria-stabilized zirconia anode substrate for tubular solid oxide fuel cells was prepared by gel casting technique. Nano-scale samaria-doped ceria (SDC) particles were formed onto the anode substrate to modify the anode microstructure by the impregnation of solution of $\text{Sm}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$. Electrochemical impedance spectroscopy, current-voltage and current-powder curves of the cells were measured using an electrochemical workstation. Scanning electron microscopy was used to observe the microstructure. The results indicate that the stability of the performance of the cell operated on humidified methane can be significantly improved by incorporating the nano-structured SDC particles, compared with the unmodified cell. This verifies that the coated SDC electrodes are very effective in suppressing catalytic carbon formation by blocking methane from approaching the Ni, which is catalytically active towards methane pyrolysis. In addition, it was found that a small amount of deposited carbon is beneficial to the performance of the anode. The cell showed a peak power density of 225 mW/cm^2 when it was fed with H_2 fuel at 700°C , but the power density increased to 400 mW/cm^2 when the fuel was switched from hydrogen to methane at the same flow rate. Methane conversion achieved about 90%, measured by gas chromatogram with a 10.0 mL/min flow rate of fuel at 700°C . Although the carbon deposition was not suppressed absolutely, some deposited carbon was beneficial for performance improvement.

Key words: Tubular solid oxide fuel cell, Gel casting, Impregnation, Methane

I. INTRODUCTION

Solid oxide fuel cells (SOFCs) represent a potential technology for clean, reliable, and flexible power production. The main advantage of SOFC is its ability to convert chemical energy directly into electrical energy without the need for combustion, giving much higher conversion efficiency than most conventional thermo-mechanical methods. Consequently, for the same power output, the SOFC has much lower carbon dioxide emissions. They also produce negligible emissions of NO_x , the main cause of acid rain and photochemical smog. In addition, the high fuel flexibility of SOFC allows a variety of fuels to be employed. There are a number of papers which have described in detail the advantages and applications of SOFC [1–5].

Although hydrogen is an ideal fuel for SOFC, there is not an established infrastructure for hydrogen processing and distribution. Natural gas, of which the main component is methane, is regarded as a relatively cheap

and popularly available fuel, and is also suitable for SOFC. However, when nature gas (or methane) is directly fed to a Ni-cermet anode, carbon deposition often takes place due to the high catalytic activity of Ni for breaking C–H bond, and this results in a rapid degradation of the anode performance and a great drop of electrical power output of cell [6,7]. There are many groups who have devoted themselves to studies on carbon deposition on Ni/YSZ (yttria-stabilized zirconia) anodes when methane fuel is directly fed [8–12].

To solve the problem of carbon deposition on the Ni-based anode, major studies have focused on the steam reforming of methane [13–18], or have applied a barrier layer such as partially stabilized zirconia (PSZ) and doped- CeO_2 [19–24].

Recently, there have been many studies directed towards the improvement of the SOFC electrodes by means of microstructure optimization by the wet impregnation. But in all the available literature, the pre-sintered porous electrodes for the wet impregnation are prepared by the tape-casting, screen printing or uniaxial pressure method for planar SOFC. Compared with the planar SOFC, the tubular SOFC is a better alternative because it is easier to seal, make into stacks and scale up. In this work, pre-sintered porous NiO/YSZ

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anode substrates for tubular SOFC were prepared by the gel casting technique. Although the extrusion technique is generally adopted for the fabrication of tubular substrates [25–27], it needs a special and expensive apparatus. The gel casting process is more cost-effective and has been used successfully to fabricate planar SOFC ceramic parts by Jiang *et al.* [28] and Huang *et al.* [29]. In the present study, we fabricated the tubular SOFC anode substrate by the gel casting technique and studied the effect of the impregnation of samaria-doped ceria (SDC) onto the anode substrate on the cycle performance of the cell alternately operated on humidified hydrogen and methane fuel, as well as the output peak power density and the stability of performance when the cell was operated on humidified methane fuel. In addition, the ratio of methane catalyzed and reformed was analyzed.

II. EXPERIMENTS

A. Preparation of tubular NiO/YSZ substrates by gel casting technique

To prepare the porous NiO/YSZ anode substrate by the gel casting technique, commercial NiO and YSZ powders were used as the starting materials and mixed in a proportion of 60%NiO and 40%YSZ. Acrylamide (AM, 16% of the powders in this study) monomer, N, N'-methylenebisacrylamide (MBAM, 2% of the powders) cross-linker, and polyacrylic acid (PAA, 5% of the powders) were dissolved in distilled water, and then the premixed NiO/YSZ powders and graphite with an average particle size of about 3 μm as pore-former were added in the solution and ball-milled for 3 h. Based on previous experiments in our laboratory [30], the pore former addition should be at least 15% of the NiO/YSZ mixture to prepare a substrate with a high enough porosity for the next impregnation. In this work, the addition was fixed at 20%. An organic material, polyvinyl pyrrolidone (PVP, Sigma-Aldrich, 5% of the pore-former), was added to keep the graphite from separating from the slurry [28]. Finally, ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, APS, 0.25% of the AM) initiator was added and ball-milled for 30 min. The slurry was deaired before being poured into a forming-mold. The mold used in the experiments consists of two glass tubes fixed coaxially on a bottom plate, the inner tube with 6.2 mm outside diameter and the outer tube with 9.5 mm inside diameter. After the slurry was poured into the mold, it was gelled by the polymerization of mono-functional AM and di-functional MBAM at 80 $^\circ\text{C}$ for 6–10 h under sealed conditions. Finally, the elastic NiO/YSZ gel-body was de-molded, dried at room temperature for 3–5 days, and fired in air at 1100 $^\circ\text{C}$ for 2 h. The heating rate was fixed at 0.5 $^\circ\text{C}/\text{min}$ below 500 $^\circ\text{C}$ and 1 $^\circ\text{C}/\text{min}$ between 500 and 1100 $^\circ\text{C}$. Then the NiO/YSZ tube with some intensity was cut into

3.5 cm in length as anode substrate of tubular SOFC.

B. Fabrication of single cells

A single cell consisted essentially of the as-prepared NiO/YSZ anode substrate, a fine NiO/YSZ anode interlayer, a thin YSZ electrolyte layer, and a $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.9}\text{MnO}_{3-\delta}$ (LSM)/ $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) composite cathode. The anode substrate is porous and it is difficult to prepare a dense thin YSZ electrolyte layer on it. Therefore, the fine NiO/YSZ anode interlayer was prepared firstly on the outer surface of the NiO/YSZ substrate by the slurry coating method [31] and then fired in air at 1150 $^\circ\text{C}$ for 2 h. The fine NiO/YSZ powders were synthesized by the co-precipitation technique. The YSZ (Tosoh, TZ-8YS) electrolyte thin layer was prepared by the dip-coating method [31]. The cycle of dip-coating and drying was repeated 3 times in our experiments. Then the green substrate with anode interlayer and thin electrolyte layer was co-sintered in air at 1350 $^\circ\text{C}$ for 5 h. The heating rate was fixed at 1 $^\circ\text{C}/\text{min}$ below 500 $^\circ\text{C}$ and 2 $^\circ\text{C}/\text{min}$ between 500 and 1350 $^\circ\text{C}$. The LSM/SDC composite cathode with an effective area of 1.0 cm^2 was prepared using a brush technique and fired in air at 1150 $^\circ\text{C}$ for 2 h. The LSM powder was synthesized by the glycine-nitrate method [32] and the SDC by the oxalate co-precipitation technique [33].

The microstructure of the tubular porous NiO/YSZ anode substrate was modified with the impregnation of SDC before the preparation of the LSM/SDC composite cathode. An aqueous solution of $\text{Sm}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$ (analytical grade, Sinopharm Chemical Reagent Co., Ltd) ($\text{Sm}^{3+}:\text{Ce}^{3+}=1:4$) was filled into the pore of the tubular substrates of the as-prepared semi-finished cell (without the cathode) under vacuum. Then the specimen was dried and fired in air at 800 $^\circ\text{C}$ for 2 h with the heating rate of 2 $^\circ\text{C}/\text{min}$. The cycle of impregnating-and-firing was repeated until enough SDC loading was achieved. The resultant SDC loading was determined by the weight difference measured before and after the impregnation treatment. A detailed description can be found in our previous work [20].

C. Cell testing

A house-made setup was used to investigate the performance of the cells. The setup involves a cell holder and a program controlled oven. A test cell was first sealed between two alumina tubes with silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins). Silver wires ($d=0.5$ mm) were used as current-collectors for both anode and cathode. The test cell was heated to 700 $^\circ\text{C}$ at the heating rate of 2 $^\circ\text{C}/\text{min}$ and then the anode NiO/YSZ was reduced to Ni/YSZ under flowing hydrogen for 8 h. Fuel bub-

bled through water maintained at a fixed temperature was fed and circulated past the anode, and ambient air was circulated past the cathode. The impedance spectra, current-voltage (I - V) and current-power (I - P) curves of the cells were measured using an electrochemical workstation (IM6e, Zahner). The impedance spectra were measured under open-circuit conditions in the frequency range of 0.1 Hz to 1 MHz with a signal amplitude of 10 mV. The microstructure was observed using a scanning electron microscope (SEM, JSM-6700F, JEOL). Analysis of the resulting gas was performed by a gas chromatograph GC9750 equipped with thermal conductivity detectors and Porapak Q column. Argon was used as a carrier gas for the reactant stream. An ice bath was set between the cell and the gas chromatograph to condense water.

III. RESULTS AND DISCUSSION

A. Cycle performance of cell operated on humidified hydrogen and methane

Figure 1 shows that the performance of as-prepared cell at a constant output voltage of 0.5 V and at 700 °C changes with the alternately fed fuels of humidified methane and hydrogen. The cell performance increases at first, and then reaches a stable value after 6 h operation on humidified methane. The increase of the cell performance accompanies carbon deposition, because the deposited carbon can modify the microstructure of the anode substrate. After the cell is kept under

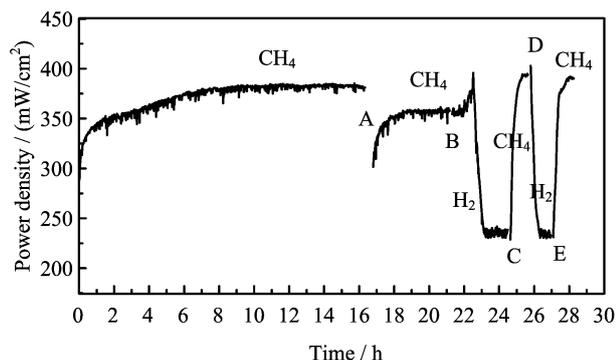
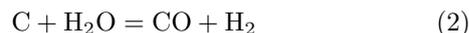


FIG. 1 The performance dependence of as-prepared cell on fed fuels of humidified methane and hydrogen at a constant output voltage of 0.5 V and 700 °C. The operation was as following sequence: at the position A, a period of 30 min, in which humidified methane was fed continuously but the circuit of cell was opened; after the period the circuit was closed again; at the point B, the fed fuel was switched from humidified methane to hydrogen and kept until C; at the point C, the fed fuel was switched from humidified hydrogen to methane again and kept until D; at the point D the cell was operated on humidified hydrogen switched from methane until the point E; from point E on, the cell was fed with humidified methane switched from hydrogen.

open-circuit conditions for 30 min (A position), the output circuit is closed again, but the performance cannot reach the same value as before. That is attributed to there being no oxygen ions present (at open circuit conditions) for the removal of carbon. It is well known that nickel is a good catalyst for cracking C-H and C-C bonds and it has been used to catalyze the formation of carbon nanofiber [34,35]. Under the anode conditions, methane could crack via the pyrolysis reaction:



When the circuit is closed, methane could be electrochemical oxidated by oxygen, and the product H_2O could help to remove the deposited carbon via steam reforming reaction:



From position B to C, the humidified hydrogen is fed and circulated past the anode, and the cell performance first increases, then decreases, and reaches a new stable value after 1 h. That accompanies the change of microstructure of the anode and the removal of deposited carbon. From then on, humidified hydrogen and methane are fed alternately, and the microstructure and performance of the anode changes alternately.

The cell performance at C and D position (Fig.1) is shown in Fig.2. When the cell is operated on hydrogen and methane, the peak power density is 225 and 400 mW/cm^2 , respectively. Deposited carbon results in the cell performance being improved by 43.8% at 700 °C. This value is considerable compared with the improvement reported by Zhu *et al.* [20]. Measured open circuit voltage (OCV) value operated on methane (~ 1.06 V) is higher than that (~ 1.02 V) operated on hydrogen, and both are close to the predicted values [36].

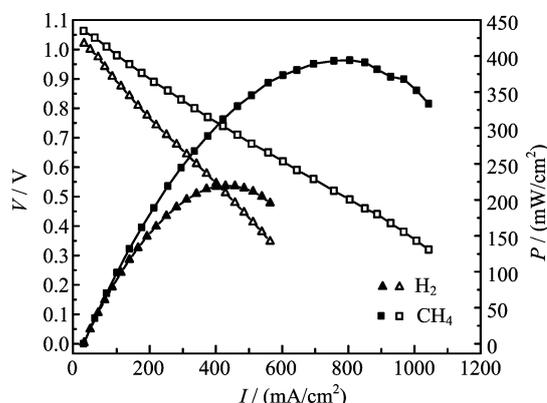


FIG. 2 Voltage and power density versus current density of gel casting Ni/YSZ anode-supported tubular SOFC operated on humidified hydrogen and methane at 700 °C, triangle for the cell fed with hydrogen and square for methane, solid for I - P and hollow for I - V curves, respectively.

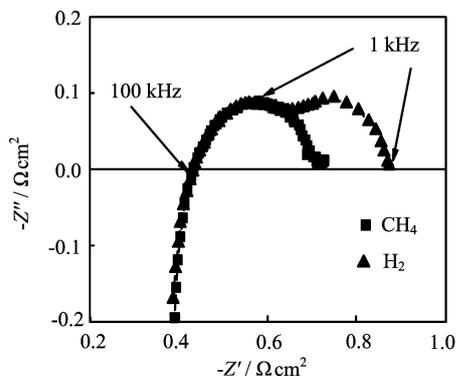


FIG. 3 Impedance spectra of gel casting Ni/YSZ anode-supported thin film YSZ tubular SOFC operated on humidified hydrogen and methane under open-circuit conditions at 700 °C. Z' is the real resistance, Z'' is the imaginary resistance.

The impedance spectra of the gel casting Ni/YSZ anode-supported thin film YSZ electrolyte SOFC operated on humidified hydrogen and methane under open-circuit conditions are shown in Fig.3. The electrolyte resistance corresponding to the high-frequency intercept is $0.43 \Omega \text{ cm}^2$, and is consistent when the cell is operated on hydrogen or methane. The overall area specific resistance determined from the difference between the high- and low-frequency intercepts is 0.44 and $0.29 \Omega \text{ cm}^2$ operated on hydrogen and methane at 700 °C, respectively. The low frequency cycle is so short that it is difficult to determine it when operating on methane. It is generally considered that the high frequency cycle corresponds to the charge exchange process (the fuel oxidation) and the low frequency cycle corresponds to the surface process, such as the adsorption and/or diffusion of reactant and the transfer of reaction production. Consequently, the performance improvement of the cell operated on methane might be mainly attributed to the deposited carbon reducing the activation energy of the fuel oxidation or improving the transfer of the fuel reaction production in the anode substrate.

B. Stability of performance operated on humidified methane at 700 °C

Figure 4 shows the stability of performance of the tubular SOFC operated on humidified methane. The performance P of the cell with unmodified anode is not stable and reduces rapidly from 350 mW/cm^2 to 150 mW/cm^2 within 24 h. In contrast, stable operation over an 80 h period was observed for the cell with modified anode. The stability of performance of the tubular SOFC is improved with impregnation of SDC. Figure 4(b) shows the stability of performance P of the tubular SOFC with modified anode substrate measured at different temperatures. The cell was operated at 800 °C, then 750 °C, and finally 700 °C. The performance re-

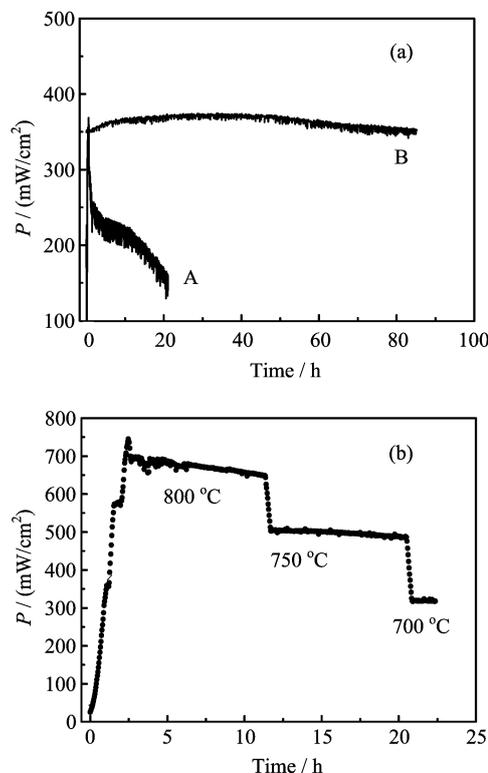


FIG. 4 Stability of performance of the tubular SOFC operated at 700 °C (a) with unmodified anode substrate A and modified anode substrate B and (b) operated at different temperatures.

duced 10.1% at 800 °C within 10 h. Therefore, the performance of the cell with modified anode is still unstable when it is operated on humidified methane at higher temperature. When the operation temperature is higher, carbon deposition is more difficult to suppress [36].

C. Morphology of anode substrates

Scanning electron micrographs of cross-section of anodes before and after exposure to methane are shown in Fig.5. Morphology of the unmodified anode after a 25 h operation on humidified methane is shown in Fig.5(a), and the surface of Ni is full of vermicular filaments. The carbon deposited on the surface or in the porous Ni, would block the contact of the fuel and the catalyzer Ni. After impregnation of SDC, the surface of the NiO and the YSZ particles of the porous substrate is covered by the very fine and well dispersed nano-scale SDC particles (Fig.5(b)). The impregnated SDC particles are connected along the surface of NiO particles, forming a pathway for oxygen ion conduction. Eventually, the triple-phase boundary (TPB) is extended beyond the anode-electrolyte interface where the electrochemical oxidation possibly takes place. After 85 h

TABLE I The resulting gas after methane oxidation reaction over the Ni/YSZ anodes with unmodified anode and modified anode.

Cell	Process	Conversion/CH ₄	Selectivity/CO	Selectivity/CO ₂
Unmodified anode	Fresh	90.3%	—	—
	After 10 h	69.6%	—	—
Modified anode	Fresh	89.7%	28.7%	71.3%
	After 10 h	89.5%	33.0%	67.0%

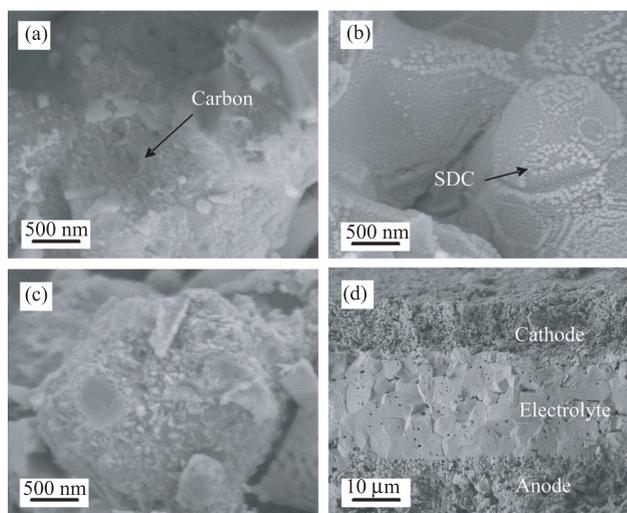


FIG. 5 Scanning electron micrographs of cross-section. (a) unmodified anode substrate after 25 h operation. (b) modified anode substrate before the reduction. (c) modified anode substrate after 85 h operation. (d) overview of cell after 85 h operation.

operation exposure to humidified methane, there is little carbon on the surface of Ni (Fig.5(c)). An overview of the tubular SOFC after 85 h operation on humidified methane is shown in Fig.5(d). The Ni/YSZ anode substrate and the LSM/SDC composite cathode ($\sim 10 \mu\text{m}$ thick) has a homogeneous porous structure and is cohering very well to the YSZ membrane ($\sim 20 \mu\text{m}$ thick). The relatively dense anode interlayer has a thickness of about $5 \mu\text{m}$.

D. Analysis of fuel reaction products

The resulting gas after methane oxidation reaction over the Ni/YSZ anodes with and without impregnation of SDC is shown in Table I. The flow rate of methane is fixed at 10 mL/min. For the anode without impregnation, the methane conversion decreases from 90.3% at the beginning to 69.6% after 10 h. The Ni/YSZ anode is deactivated by the carbon that forms around the surface of Ni (Fig.4(a)). When the impregnated anode is tested, although the selectivity of CO₂ decreases a little, the conversion of methane stayed at a stable level of about 90%. The coating of nano scale SDC particles effectively prohibited the anode from deactivation

(Fig.4(b)).

IV. CONCLUSION

A porous NiO/YSZ anode substrate for tubular SOFC was successfully prepared by the low cost gel casting technique and the anode substrate was modified by wet impregnation method. The performance of the cell with impregnation of SDC was stable when it was operated on humidified methane at 700 °C. Excessive carbon deposition was effectively suppressed. Small amounts of deposited carbon did not destroy the anode substrate, and, in fact, improved the performance of the cell from 225 mW/cm² (H₂) to 400 mW/cm² (CH₄) at 700 °C. Most of the methane fuel took part in the catalyzed reaction, and the conversion of methane kept at a stable level of about 90%.

V. ACKNOWLEDGMENTS

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