

Direct Power Generation from Low Concentration Coal-Bed Gas by a Catalyst-Modified Solid Oxide Fuel Cell

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Clear utilization of low-concentration coal-bed gas (LC-CBG) would save energy, mitigate greenhouse gas emissions, and reduce explosion accidents during a coal-mining process. In this paper, a novel catalyst Ni/BaO/CeO₂ (NBC) is developed for CH₄ partial oxidation and is used as an independent catalyst layer of a Ni cermet anode. LC-CBG with composition of 30% methane and 70% air is directly fed to the catalyst-modified SOFC to generate electricity. Operated on 30% LC-CBG, the NBC-modified cell shows better performance and discharge stability

1. Introduction

With energy shortage and global warming potential (GWP), coal-bed gas (CBG), a byproduct of the coal formation process, has been recovered all over the world as a clean energy source. Historically, CBG was considered a safety hazard in the process of coal mining. Therefore, "degasification of the coal bed prior to mining" has been a key step to alleviate the safety threat in coal-mining production. Depending on the degasification method employed, the methane content varies in the range of 3~100%. The medium- and high-quality CBG (more than 30% of methane concentration) have shown a large variety of applications, such as fuels for industries, civil use or power generation. Low concentration coal-bed gas (LC-CBG) is dangerously explosive if the methane content lies in a range between 5% and 16%. On considering safety, gases containing methane below 30% are not advised to be utilized, which are burned out or vented. However, methane is a greenhouse gas, which

than the conventional cell without the catalyst layer. Gas chromatography (GC) analysis on effluent gases extracted from the operating catalyst-modified cells also indicates a higher CH₄ conversion when the cell is fed with 30% LC-CBG than when fed with 3% H₂O-humidified methane. Post-mortem microstructures of cell surface were analyzed. The NBC-modified cell has a potential application for fuels containing low concentration methane and air.

has about 25 times more emission than CO2.[1] Therefore, LC-CBG emission not only wastes energy, also increases the greenhouse effect. In recent years, power generation using LC-CBG is thought to be one of best utilization methods. Currently, power generation technology using 10% LC-CBG has been realized in China. However, the state administration of coal mine safety of China made some limitation for the establishment of LC-CBG power generation: (1) the drainage amount of LC-CBG is at least 1 million cubic meters per vear; (2) the methane content ranges 6-25%. Thus, power generation using LC-CBG is applied only in the mining areas with high LC-CBG production and constant methane content. In addition, current power generation using LC-CBG utilizes conventional internal combustion (IC) engines, steam turbines and gas turbines with energy conversion from chemical energy to thermal energy to mechanical energy and last to electricity, which is in low conversion efficiency limited to the Carnot cycle. But also, these projects need a large initial investment accompanied with a long construction period.

Fuel cell can generate electricity with high efficiency and low emission. Compared with low-temperature fuel cells, the greatest advantage of solid oxide fuel cells (SOFCs) is fuel flexibility. Theoretically, all carbonaceous species can be used as SOFC fuels with the electrochemical oxidation products CO_2 and H_2O . In addition, SOFC is modularly assembled. Therefore, the electrical output is controllable from tens to thousands of watts according to gas supply and power consumption. SOFC would provide an alternative way for LC-CBG utilization.

However, when LC-CBG containing methane below 30% (O/ C > 0.98) is directly fed to the state-of-art SOFC with a Ni–yttriastabilized zirconia (YSZ) anode, the Ni cermet anode would inevitably be oxidized and deactivated.^[2] Simultaneously, sintering of Ni particles would happen because of the local elevation of temperature caused by the exothermic internal MPO reaction.^[3] Lee reported that an O/C ratio of 0.8 is the best

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dilution of methane by air from the aspects of both performances and material degradation.^[2c] Therefore, for direct utilization of LC-CBG, the Ni-YSZ anode has to be modified. Using a Ni–Gd₂O₂-doped CeO₂ (Ni–GDC) anode-supported SOFC, a high power density and stability over 500 h are achieved.^[2c] However, due to the electro-conductivity of CeO₂, OCV of the cell is very low, which is unbeneficial to practical application. In addition, Ni–GDC anode has a relative low mechanical strength.^[4] In this paper, a novel catalyst for methane partial oxidation/reforming is developed and is fabricated over the Ni-YSZ anode. Before reaching the anode surface, most of LC-CBG has been converted to H₂, CO and CO₂ by reforming or partial oxidation.^[5] As we know, hydrocarbon reforming/oxidation is accompanied with heat absorbing/releasing. When the catalyst layer is directly deposited on the anode surface, the reaction heat from CH₄ reforming/oxidation would lead to temperature gradients within the cell, causing a cell geometric integrity issue. In this case, the application of a barrier layer over an anode layer would enhance cell stability.^[6] In addition, the mismatch in TECs between catalyst and anode materials is also a big concern. In our recent paper,^[7] we reported a new strategy to increase the coking-resistant ability of a Ni-based anode by applying an independent catalyst layer. Such cell configuration can reduce any potential damage from the thermal-mechanical stress.

Ni-based catalysts usually show very high catalytic activities for methane partial oxidation (MPO), methane steam reforming (MSR) and methane dry reforming (MDR). However, lots of researches have demonstrated rapid deactivation for a Ni-based catalyst during methane partial oxidation/reforming reaction, mainly due to the loss of Ni active sites blocked by deposited carbon (or coking) and the sintering of Ni particles.^[8] CeO₂ has been reported to effectively suppress carbon deposition in a hydrocarbon atmosphere due to the mobile lattice oxygen in CeO₂, originated from the change of oxidation states of cerium between +3 and +4.^[9] Yang reported that adding cerium to a Ni-based catalyst actually restrained the crystalline growth of NiO particles.^[10] However, Pantaleo reported 6 wt.% Ni-containing CeO₂ catalyst still experienced coking during MPO test with an O/C ratio of around 1.[11] Ideris reported that carbon deposition was still observed on a Ni-SDC anode exposure to dry CH₄.^[12] These results suggest further modifications for the Ni-CeO₂ catalyst are required in order to realize coking-free operation on methane-based fuels. Alkali earth metal oxides such as BaO, CaO and SrO have shown good coking resistance because of their strong water-affinity.^[13] For example, by incorporating 2.25 wt.% CaO into a Ni-Sm₂O₃-doped-CeO₂ (SDC) anode, much improved stability was achieved when operating on hydrocarbon fuel.^[13c] A MgO loading of 2.5 wt.% in a Ni-SDC anode improved the cell stability to 330 h in humidified methane.^[9h] Walker reported that 1 wt.% BaO infiltration to a Ni cermet anode inhibited carbon deposition on the anode.^[13g] From the discussion above, it can be speculated that co-modification of a Ni-based catalyst by an oxygen storage carrier and alkali earth metal oxides may be an effective way to suppress coking when hydrocarbon fuels are used.

In present work, a novel Ni-based catalyst (BaO and CeO_2 co-modified nickel, NBC) for methane partial oxidation/reform-

ing is prepared and fabricated as an independent catalyst layer for a SOFC anode. This Ni-based catalyst shows a superior activity for MPO, MDR and MSR. Considering safety and power generation efficiency, a simulation of 30% LC-CBG is considered. That means an O/C ratio of 0.98 is applied, which is basically in line with the stoichiometry of MPO [Eq. (1)].

$$2CH_4 + O_2 = 2CO + 4H_2$$
(1)

When fed with 30% LC-CBG, the NBC-modified cell shows better electrochemical performance and stability than the conventional cell without the catalyst layer. Because no any sulfur compound is detected in local LC-CBG, sulfur poisoning to Ni cermet anode is not be considered in this paper.

2. Results and Discussion

2.1. Structural Properties of the Catalyst

Methods commonly used to prepare Ni-containing catalysts include (co)impregnation, in situ-reduction of Ni-doped perovskites and gel-combustion. However, (co)impregnation is uncontrollable for an even distribution of the infiltrated phase. For in situ-reduction of perovskites, although some perovskites can produce a dispersive metallic phase, some stable perovskites, like LaNi_{1-x}Al_xO₃,^[14] are difficult to be reduced and are not suitable as catalyst support. Gel-combustion, especially glycine combustion, can evenly mix the raw materials at molecular levels, allowing a lower calcination temperature for a finer particle size.

XRD pattern for the as-prepared oxidized-NBC(ONBC) powder is shown in Figure 1a, which suggests a physical



Figure 1. X-ray patterns of (a) as-sintered ONBC and (b) the reduced NBC.

mixture of crystalline phase of CeO_2 and NiO. No any diffraction peak assignable to BaO crystalline phase is detected. Probably amorphous BaO forms. The average crystalline size of CeO_2 and NiO phase is ~22 nm and ~31 nm, respectively, as estimated



from the half width of the diffraction peaks at 2θ of 28.5° and 43.3° , respectively, according to the Scherrer equation.

Under SOFC operating conditions fed with H_2 or CH_4 , ONBC is in a reducing atmosphere. Therefore, the structural information of the in situ-reduced NBC powder is also obtained by XRD (Figure 1b). After the powder was treated under a H_2 atmosphere at 800 °C for 2 h, fluorite structure of CeO₂ is retained. The peaks assigned to NiO disappear. Simultaneously, two diffraction peaks appear which are located at 2 θ of 44.5° and 51.9° and are assigned to metallic Ni, suggesting that NiO is reduced to metallic Ni with an average particle size of 18 nm. Ever Ermakova et al. reported that coking had a strong correlation with the Ni particle size, and a nickel particle size between 20 and 60 nm caused the most serious coking.^[15] Therefore, it is anticipated that NBC in this work has a good coking resistance.

2.2. Texture Properties of Catalyst Layer and Morphological Structure of Cells

Usually, for a catalyst, the larger is the specific surface area, the higher the catalytic activity is. As a catalyst layer of SOFC anode, a large number of pores are also of the essence for fuel gas transporting. The micropores in the catalyst layer mainly come from the pore former and the interspace between the Ni particles due to the volume shrinkage from NiO to Ni. However, a small pore size is required to ensure full contact of CH₄ with catalyst and to avoid CH₄ passing directly without conversion. Herein, pore parameters and the specific surface area of the NBC–Al₂O₃ slice were determined using N₂ physical adsorption. The BJH pore volume is 0.2 cm³g⁻¹. The BET surface area is 65.5 m²g⁻¹. The isotherm shows a typical type-H3 hysteresis loop (Figure 2), indicating a mesoporous structure. The pore



Figure 2. Nitrogen gas adsorption/desorption isotherm for the NBC– AI_2O_3 catalyst layer. The inset is the pore size distribution of the sample.

size distribution curve is broad with an average pore-diameter of ca. 12.4 nm, much smaller than the reported PSZ barrier layer with a pore radius of $0.4 \ \mu m$.^[6] Therefore, the double-layered

catalyst slice also acts as a barrier layer which partially impedes the flux of fuel into the Ni cermet anode.

It is well known that the tighter is the contact interface between electrolyte and electrode, the smaller the contact resistance is. From the cross-sectional SEM images of cell in Figure S1a, both anode and cathode layers are highly porous and contact tightly with the dense electrolyte layer. A porous double-layered catalyst is constructed by 80 μ m catalyst layer and 110 μ m substrate layer (Figure S1b). The top-view SEM image (Figure S1c) of a fresh NBC catalyst layer shows that nano-scale catalyst particles are distributed evenly with a high porosity. The geometry of the cell tested is listed in Table 1.

Table 1. The geometry of the cell tested.					
	Anode	Electrolyte	Cathode	Substrate	Catalyst
	layer	layer	layer	layer	layer
Thickness [µm]	500	23	6	110	80
Porosity [%]	38	-	40	56	56

2.3. Catalytic Performance of NBC for MPO, MSR, and MDR

Metal Ni and CeO₂ have been reported to high-efficiently catalyze steam reforming,^[16] partial oxidation^[17] or CO₂ dry reforming^[18] of hydrocarbon fuels. Under a H₂ atmosphere, ONBC would be reduced to produce Ni and CeO₂. Therefore, the in situ-reduced NBC is expected to have high catalytic performance for CH₄ reforming/partial oxidation reactions. The catalytic performances of NBC powder for MPO (V_{CH4}:V_{O2}, 2:1), MSR (V_{CH4}:V_{H2O}, 1:1) and MDR (V_{CH4}:V_{CO2}, 1:1) are shown in Figure 3. As expected, NBC shows the highest catalytic activity



Figure 3. CH₄ conversion and CO selectivity of the in-situ reduced NBC powders for MPO with a CH₄–O₂ (V/V, 2:1) mixture, for MSR with a CH₄–H₂O (V/V, 1:1) mixture and MDR with a CH₄–CO₂ (V/V, 1:1) mixture in the range of 600–900 °C.

towards MPO. The CH₄ conversion efficiency reaches 100%, 99.4% and 97.4% at 850°C, 800°C and 750°C with CO selectivity of 92.4%, 90.3% and 89.6%, respectively. For MSR, the CH₄ conversion efficiency is 84%, 75% and 66% at 850°C, 800°C and 750°C with CO selectivity of 98%, 95% and 91%,

respectively. For MDR, the CH₄ conversion efficiency is 74%, 71% and 58% at 850 °C, 800 °C and 750 °C with CO selectivity of 94%, 91% and 83%, respectively. That means that NBC has the highest activity for MPO, followed by MSR>MDR. The relative high CH₄ conversion under low oxygen concentration provides NBC a possibility of acting as a SOFC anode catalyst.

2.4. Single-Cell Performance Fed with 30% LC-CBG

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Catalytic activity tests have shown that NBC has high catalytic activity for MPO. The catalyst-modified cell (NBC–Al₂O₃//Ni–YSZ) is used to evaluate the power generation ability using 30% LC-CBG. The cell performance is related with flow rate of fuel. As shown in Figure S2, PPD of NBC–Al₂O₃//Ni–YSZ increases with the flow rate until the flow rate reaches 50 ml min⁻¹. PPD keeps nearly constant at a flow rate from 50 to 100 ml min⁻¹. Probably, a low flow rate causes a large fuel diffusion polarization. In the following tests, a flow rate of 80 ml min⁻¹ is used. A conventional cell with Ni–YSZ anode (Ni–YSZ) is used for comparison. Figure 4 and Figure S3 shows the corresponding electrochem-



Figure 4. /–V (P) polarization curves of Ni–YSZ (a) and NBC–Al₂O₃/Ni–YSZ (b) using 30% LC-CBG at various temperatures from 750 $^\circ$ C to 850 $^\circ$ C.

ical performance of cells with and without the NBC catalyst layer at various temperatures. Due to the oxygen pressure in anode, OCVs fall to near 1 V. For Ni–YSZ, the PPDs are 0.20, 0.31, 0.46 W cm⁻² at 750, 800 and 850 °C, respectively. While for NBC–Al₂O₃//Ni–YSZ, the PPDs are 0.31, 0.44 and 0.60 W cm⁻² at the corresponding temperature, respectively. NBC–Al₂O₃//

Ni–YSZ shows a 30% increment of PPD and a 46% increment of the maximum current density at $850^{\circ}C$ compared with Ni–YSZ (Figure 5a). Both the cells show an insufficient fuel



Figure 5. The comparison of I-V (P) (a) and EIS(b) of NBC-Al₂O₃//Ni-YSZ and Ni-YSZ using 30% LC-CBG at 850 °C.

supply at high current densities with downward-bending I-V curves, probably which is due to the dilution of fuels by the inert N₂ in air. EIS under open-circuit condition (Figure 5b) also shows a different electrode process between NBC-Al₂O₃// Ni-YSZ and Ni-YSZ. Usually, total electrochemical impedance includes polarization resistance (R_{o}) and ohmic resistance (R_{o}) . $R_{\rm o}$ is mainly related with the ionic resistance from the electrolyte and the electronic resistance from the electrode, which is approximately the high frequency intercept of the impedance curve on the real axis. While R_{p} is corresponded to the difference between intercepts of the impedance arc on the real axis, which involves the non-charge transfer process in the lowfrequency domain, and the charge transfer process in the highfrequency domain. It is clear that the whole resistance of the two cells is dependent on R_p. NBC-Al₂O₃//Ni-YSZ shows a smaller R_p than Ni–YSZ. The line at low frequencies of EIS clearly indicates a diffusion-controlled electrode process with an upfolding line, which is related to gas-diffusion, adsorption and dissociation. For Ni-YSZ, the Nyquist plot shows one semicircle, and the Bode plot shows a large capacitance response with the summit frequency at 312 Hz. While for NBC–Al $_2O_3/\!/$ Ni-YSZ, the Nyquist plot clearly shows two semi-circles: the first circle at higher frequencies is attributed to activation losses,



while the second circle at lower frequencies is concerned with mass transfer limitation.^[19] The Bode plot shows a less capacitance response with the summit frequency at 110 Hz, indicating a less diffusion resistance. The observed decrease of activation and diffusion polarizations in EIS experiments suggests that the composition of fuels in SOFC anode is H₂ or CO derived from CH₄ conversion. As shown in [Eq. (1)], for MPO reaction, one CH₄ molecule produces two H₂ molecules and one CO molecule, which means the concentration of effective fuels increases after MPO.

2.5. Ageing Tests in Galvano-Static Mode When Feeding the Cell with 30 % LC-CBG

To examine the operation stability of the catalyst-modified cells over time when feeding the cell with 30% LC-CBG, NBC-Al₂O₃// Ni-YSZ was operated in galvanostatic mode at 800 °C with a current load of 320 mA cm⁻². A high stability with an average voltage drop of $6.37*10^{-4}$ V/h over 55 h is observed (Figure 6).



Figure 6. Time-dependent voltage of NBC–Al₂O₃//Ni–YSZ and Ni–YSZ operated on 30% LC-CBG under a constant current load of 320 mA cm⁻² at 800 $^\circ$ C.

While Ni–YSZ shows an expected voltage decay after exposure to 30% LC-CBG for 4 h. Probably, for NBC–Al₂O₃//Ni–YSZ, there are at least three explanations as followings. First, oxygen in air directly prevents instant coking because of the carbon combustion reaction. Second, due to the MPO reaction, methane is consumed, thus the methane content near anode is lowered greatly. Third, with the process of electrochemical reaction of hydrogen and CO, more and more oxygen-bearing reaction products are produced which are also beneficial to coking resistance. The long-term stability of cell with 30% LC-CBG is attributed to the high catalytic performance of NBC for MPO. Probably the gradual voltage decay is caused by the heat instability or the coarsening of anode particles and catalyst particles themselves.

2.6. GC Assay on Effluent Gases

The catalytic activity was achieved in the fixed-bed experiments with NBC powders. Usually, the desired gas hour space velocity (GHSV) for the catalytic reactions cannot be achieved in the electrode of SOFCs which gives rise to much lower utilization of fuels and conversion than those from the flow reactor. Herein, the actual catalytic behaviours of NBC during the SOFC operation are revealed. GC assay of effluent gases, which were extracted from the operating NBC-modified cell fed with 30% LC-CBG or wet CH_4 at 800°C under a different current load, reveals the chemical partial oxidation / reforming of methane (Figure 7). The results indicate that the cell fed with 30% LC-



Figure 7. GC analysis results for effluent gases extracted during operation of NBC–Al₂O₃//Ni–YSZ at 800 $^{\circ}$ C fed with 30% LC-CBG and wet CH₄.

CBG shows a 49.6% of CH₄ conversion at a 0.16 A of current load, which is higher than the cell fed with wet CH4 with a 21.7% of CH₄ conversion under the same condition. It is noteworthy that the content of CO and CO₂ in effluent varies with the applied current load. The more is the current load, the less CO is detected, and the more CO₂ is produced, which reveals that more CO is electrochemically consumed into CO₂ with increasing the current load. Probably, the decrease of CO content is also due to the water gas shift (WGS) reaction between CO and H₂O which convert CO into CO₂ because more H_2O is produced under an increased current load. $^{\ensuremath{\scriptscriptstyle [20]}}$ What deserves to be mentioned that although CH₄ conversion is higher for cell fed with 30% LC-CBG, CO selectivity in effluent gases is less than that fed with wet methane, which indicates that in the reaction of 30% LC-CBG, CH₄ molecules are oxidized into CO and CO₂, while for cell fed with the wet methane, most of CH₄ molecules are reformed into CO and H₂. For example, at a 0.16 A of current load, CO selectivity is about 49.7% for cell fed with 30% LC-CBG, while about 95.8% of CO selectivity is observed for that fed with the wet methane. These observations indicate a higher CH4 conversion when cell is fed with 30% LC-CBG than that fed with 3% H₂O-humidified methane.

The thickness of the catalyst layer is concerned with the cell performance. A thick layer will influence the gas diffusion. A thin layer will lower the CH_4 conversion. In our paper, when an

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80 μ m of thickness is used, CH₄ conversion is 49.6% and 21.7% for 30% LC-CBG and wet methane at a constant current of 0.16 A at 800 °C, respectively, which seems much lower than those in the fixed-bed reactor. Therefore, a moderate thickness of the catalyst layer still need to be modulated.

2.7. Post-mortem Microstructural Analyses of Cells

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The further characterization of the cell surface after ageing test operating on 30% LG-CBG was conducted. A fresh Ni-YSZ anode surface is provided for comparison (Figure 8a). For



Figure 8. Top-view of (a) a fresh Ni-YSZ anode layer and (b) the anode layer and (c) the catalyst layer of NBC-Al_2O_3//Ni-YSZ after ageing test fed with 30%LC-CBG.

NBC-Al₂O₃//Ni-YSZ, coarsening and sintering of Ni particles (Figure 8b) on the anode surface are clear although the porous morphology is remained. The catalyst particles also show obvious aggregation after ageing test (Figure 8c) compared with a fresh in situ-reduced catalyst surface in Figure S1c, which is unbeneficial to the stability and the activity of catalyst.

EDX analysis (Figure 9) on the anode surface of NBC-Al₂O₃// Ni-YSZ was carried out after ageing test operating on 30% LC-CBG. Because the EDX samples are easy to be contaminated by carbon, the carbon content of the anode surface of a fresh cell without exposure to 30% LC-CBG was about 7 wt%, which is



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Figure 9. EDX profiles of different anode zones of NBC-Al₂O₃//Ni-YSZ after ageing test.

similar with the literature.^[5b] The detected carbon content near Ni surface of NBC-Al₂O₃//Ni-YSZ is about 5.49. While the carbon content near YSZ particle of NBC-Al2O3//Ni-YSZ is about 7.49. These data indicate that no coking occurs on the Ni cermet anode for NBC-Al₂O₃//Ni-YSZ. These results strongly suggest that applying the NBC catalyst layer greatly improves coking resistance of a Ni-cermet anode when operating on 30% LC-CBG.

2.8. Catalytic Mechanism of NBC

Due to the reducible activity, CeO₂ plays a synergistic effect with metal Ni on the methane partial oxidation/reforming. Under a reduction atmosphere, Ce⁴⁺ is easily reduced to Ce³⁺ accompanied with the release of oxygen vacancies,^[20b] which has a strong electron donating and adsorption capability. Small molecules like CO, CH₄ or H₂O can be adsorbed and activated. It was reported that the catalytic oxidation of methane on metal oxides follows the MVK mechanism, which is characterized by the adsorption of methane molecules and the reaction with the surface lattice oxygen in oxide.^[1]

For 30% LC-CBG, the molar ratio of CH_4 to O_2 is about 2.1, which is suitable for a stoichiometric MPO reaction [Eq. (1)]. When 30% LC-CBG is fed, MPO reaction and probably, CH₄ cracking reaction occur on the Ni-based catalyst. [Eq. (2)]. Wei reported that CeO₂ as an oxygen carrier shows a high catalytic activity for MPO to produce syngas.^[21] Larrondo also showed that CeO2-contaning substrate contributes to the removal of carbonaceous deposits from Ni phase.^[22] Under SOFC condition, the water gas shift (WGS) reaction between CO and H₂O also occurs because large amounts of H₂O are produced from the electro-catalytic oxidation of H2.[20] In addition, BaO has a superior water storage capability, which is favourable for coking suppression as [Eq. (4)].^[23] With the proceeding of electro-



chemical oxidation of H_2 and CO, more H_2O and CO_2 are produced. Methane steam/dry reformations [Eqs (3) and (4)] are accelerated. ^[24] The deposited carbon is also removed with the reaction of [Eq. (5)].

$$\mathsf{CH}_4 = \mathsf{C} + 2\mathsf{H}_2 \tag{2}$$

 $CH_4 + H_2O = CO + 3H_2$ (3)

 $CH_4 + CO_2 = 2CO + 2H_2 \tag{4}$

$$C + H_2 O = CO + H_2 \tag{5}$$

As above all, NBC has a highly catalytic performance for methane reforming/partial oxidation. The high reducibility and oxygen storage/release capacity of CeO_2 , and the water-affinity of BaO allow the carbonaceous deposits to be continuously removed from the active sites of catalyst.

3. Conclusions

A new catalyst NBC for methane partial oxidation/reforming with high efficiency is developed and used as an independent catalyst layer for a Ni cermet anode. Fed with 30% LC-CBG, the NBC-modified cell shows higher electrochemical performance and stability than the conventional cell without the catalyst layer.

For an actual application, some measures must to be taken to improve the heat stability of catalyst and anode materials at high temperature. From the assay on effluent gases, it can be known that the over-oxidation of CH_4 to CO_2 occurs when 30% LC-CBG is used, which decreases the power generation efficiency. Catalyst with a higher CO selectivity should be developed. In view of the high catalytic activity of NBC for MPO, LC-CBG, which contains less than 30% methane and more than 70% air, would have a promising prospect of application as SOFC fuel, which not only saves energy, also decreases the greenhouse effect.

Experimental Section

Materials and Powder Preparation

Nano-scale NiO powder and YSZ powder were purchased from Chengdu Shudu Nanomaterials 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. Ag paste was purchased from Shanghai Research Institute of Synthetic Resins. ONBC (NiO/BaO/CeO₂, 13:2:85, wt.%) powder was prepared via a glycine combustion method as follows. Dissolving the calculated amount of barium nitrate, nickel nitrate and cerium nitrate into deionized water with stirring and heating to form solution A. Then adding glycine solution to the above solution A with the molar ratio of glycine: M^{n+} controlled to be around 3. Then the final solution was stirred continuously for 2 h to make metal ions to fully chelate with glycine. The residue after deflagration was heated at 250 $^\circ\text{C}$ for 8 h and calcined in air for 2 h at 850 $^\circ\text{C}.$

Catalyst Layer and Cell Fabrication

Al₂O₃ was used as the substrate to improve the mechanical strength of the catalyst layer. The double-layered catalyst slice was achieved by standard dry co-pressing method. The substrate powders with Al₂O₃ and polyvinyl butyral (PVB) in a ratio of 9:1 by weight were mixed homogeneously in ethanol. After dried and milled, the powder (0.3 g) was pressed using a mould (Φ 13 mm) under 144 MPa. Then 0.03 g evenly mixed powders with ONBC and PVB in a ratio of 9:1 by weight was homogenously distributed on the substrate surface then co-pressed under pressure of 240 MPa. The obtained double-layered slice was sintered in air at 850 °C for 4 h with a ramp rate of 5 °C min⁻¹.

Anode-supported cells (NiO–YSZ/YSZ/LSM–YSZ) were fabricated via a dual dry-pressing/co-sintering/wet spray-painting of LSM, and final sintering route, which is similar with our reported paper ^[7] unless 0.02 g YSZ was applied as electrolyte in this work. First, 0.25 g anode powder (NiO:YSZ=6:4, wt.%) was uniformly mixed and pressed for 30 s at 110 MPa in a steel mould (15 mm diameter). Then 0.02 g YSZ powder was tiled evenly on the anode surface and was co-pressed at 180 MPa. The formed double-layered slice of anode/electrolyte was co-sintered at 1400 °C for 5 h. Last, the cathode slurry LSM–YSZ (7:3, wt.%) was painted on the YSZ electrolyte surface with an effective area of 0.48 cm⁻². The whole cell was sintered at 1100 °C in air for 2 h. Silver wires were stuck to the anode surface and the cathode surface, respectively.

Catalyst-modified cell was assembled according to the following steps. First, the above obtained double-layered catalyst slice was put onto one end of the test quartz tube and fixed by a little of silver paste; then the button cell was placed above the catalyst slice with the cathode side outside, followed by sealing by silver paste. Diluted silver paste was painted on the cathode surface to collect current.

Characterization Techniques

X-ray diffraction (XRD) tests of the as-sintered ONBC and the reduced NBC powders were carried out on a Rigaku D/Max-RB diffractometer with a Cu K α radiation) in the range of $2\theta = 10-80^{\circ}$. The particle size was estimated using the Debye–Scherrer equation. The microstructural morphologies were recorded using a FESEM (JSM-7001F, JEOL). The semi-quantitative analysis of element contents was conducted by an energy-dispersive X-ray (EDX) spectroscopy (Bruker).

 N_2 adsorption/desorption isothermal experiments were carried out by a Micromeritics ASAP-2460 M automated surface area and pore size distribution analyzer (Micromeritics, USA) at 77 K after degassing for 24 h. The BET specific surface area, the pore size distributions and the BJH pore volume of the sample were obtained. The porosity of anode layer and catalyst layer were detected using mercury intrusion method, respectively. The porosity of cathode layer was estimated based on the cross-sectional SEM images of cell.

The fabricated cells were in situ-reduced in a H₂ atmosphere for 2 h at 700 °C. OCV was monitored until it was stable. The flow speeds of fuel at anode are 80 mlmin⁻¹(STP) for I–V tests and 15 mlmin⁻¹ (STP) for ageing tests in galvanostatic mode, respectively. The oxidant gas at cathode is surrounding air. Gas was quantified by mass flow controllers. Effluent gases entered a gas chromatograph (Agilent 7820) for on-line analysis. All of the electrochemical



performances were measured through an electrochemical workstation (lvium Technologies B.V., Netherlands) at temperatures of 750~850°C with a 50°C interval. The electrochemical impedance spectra (EIS) were obtained under open circuit voltage within a frequency range of $10^{-1} \sim 10^5$ Hz with an alternate current amplitude of 10 mV. The conventional cell with a Ni–YSZ anode without the catalyst layer and the catalyst-modified cell are designated "Ni–YSZ" and "NBC–Al₂O₃//Ni–YSZ", respectively.

Catalytic Activity Test

The catalytic activity tests for the in situ-reduced NBC powder for MPO, MSR and MDR were carried out in a tubular fixed-bed reactor at temperatures of 600~900 °C with a 50 °C interval. 0.2 g NBC powders (40–60 mesh) were evenly mixed with 0.4 g quartz sand. Then the mixture was put in the middle of the reactor and was reduced in a H₂ atmosphere at 700 °C for 2 h. The reactants, CH₄–O₂ (V/V, 2:1), CH₄–H₂O (V/V, 1:1) or CH₄–CO₂ (V/V, 1:1) flowed in the reactor from the top of the tube. The flow speed of CH₄ was controlled to be 10 mL min⁻¹ (STP). Effluent gases flowed into a gas chromatograph (Agilent 7820) for on-line analysis. A Poraplot Q, a 5 Å sieve molecular column, a Hayesep Q and a TCD were used to separate and detect CO₂, CO and CH₄. CO selectivity (%) and CH₄ conversion (%) were obtained based on the following formula, respectively:

CO selectivity (%) =
$$\frac{C_{co}}{C_{co}+C_{co2}} \times 100\%$$
 (1) (6)

$$CH_{4} \text{ conversion } (\%) = \frac{C_{co} + C_{co2}}{C_{co} + C_{cH4} + C_{co2}} \times 100\%$$
(7)

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cermet · coal-bed gas · energy conversion · fuel cells · supported catalysts

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