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Direct Operation of Solid Oxide Fuel Cells on Low-Concentration **Oxygen-Bearing Coal-Bed Methane with High Stability**

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ABSTRACT: This paper studies the electrochemical feasibility of the direct conversion of low-concentration, oxygen-bearing coal-bed methane (CBM, 30 vol % CH_4) to electricity via solid oxide fuel cells (SOFCs). A fuel cell with the LiLaNi–Al₂O₃/Cu catalyst layer was developed, and a maximum power output of ~ 1068 mW cm⁻² was achieved at 850 °C using 30 vol % CBM fuel, which is only modestly lower than that from a cell based on hydrogen fuel. The stability test showed that the cell operation was quite stable during the 120-h test period, which is ~40-fold longer than that of the cell without catalyst layer. The partial oxidation of methane (POM) occurring in the anode may play an important role when using 30 vol % CBM fuel, which not only supplies highly active gaseous fuels (H₂ and CO) but also suppresses the carbon deposition on the anode. By modifying the anode with a LiLaNi-Al₂O₃/Cu catalyst layer, the POM of 30 vol % CBM was further promoted and the carbon deposition over the anode was mitigated more efficiently. Therefore, the strategy of direct conversion of low-concentration, oxygen-bearing CBM via the SOFCs with an anode catalyst layer may pave an alternative way to utilize this abundant resource efficiently and cleanly.

1. INTRODUCTION

Recently, coal-bed methane (CBM) has received growing attention worldwide for its potential as a clean energy source.¹⁻³ CBM is a mixture of methane and other contaminants $(N_{2i}, O_{2i}, etc.)$ released from the coal seam and surrounding rock strata, in association with mining activities. As the principal energy carrier of CBM, methane has a high calorific value (55.7 MJ kg⁻¹) and the highest hydrogen-tocarbon ratio in hydrocarbons; thus, it is inherently a clean and valuable fuel source. On the other hand, methane is the second most important greenhouse gas after CO₂ with a global warming potential (GWP) of 25 times that of CO₂ over a period of 100 years.⁴ The atmospheric methane concentration accounts for $\sim 20\%$ of the total anthropogenic greenhouse gas emissions.⁵ Coal mining accounted for 8%-10% of the global anthropogenic methane emissions in 2015, and the emission is predicted to rise by 15% by 2020.^{6,7} So, CBM emissions result not only in a waste of energy but also in an environmental hazard. Therefore, the substantial reduction of CBM emissions and efficient utilization of CBM are critically important to meet the increasing energy demand and to mitigate climate change.

CBM with a minimum of 95 vol % CH₄ normally qualifies to be injected into natural gas pipeline for sale; otherwise, purification processes (nitrogen rejection, deoxygenation, etc.) prior to pipeline injection are required. In fact, the purification for low-concentration CBM ($<40 \text{ vol } \% \text{ CH}_4$) is unlikely to be practical, with regard to both cost and technique.⁶ Fortunately, power generators can directly use CBM with 30-40 vol % CH₄ to generate electricity. In addition, most coal mines have significant electricity loads, which makes the on-site CBMbased power generation more attractive. However, the major combustion-based power generation technologies, such as internal combustion engines and conventional turbines, operate on methane-based fuels generally at efficiencies in the range of <30% and with certain environmental impact.⁸

Solid oxide fuel cells (SOFCs) are electrochemical devices that directly convert chemical energy in fuel to electricity in a high-efficiency and low-emissions manner.⁸⁻¹⁰ Fuel flexibility is another distinguishing advantage of SOFCs, which endows SOFCs great application value for converting various practical fuels, such as natural gas, coal gas, syngas, biomass gasification product gases, and solid carbons (biochar, coalchar, etc.).^{8,11–15} Without the limitation of a Carnot cycle related to combustion process, SOFCs promise to improve the conversion efficiency of methane to >60%.⁸⁻¹⁰ Meanwhile, this conversion process emits virtually zero nitrogen oxide (NO_x) and particulate matter, and it significantly reduces CO_2 emissions. NO_x is another greenhouse gas with a GWP 298 times that of CO₂ over a period of 100 years, and causes severe environmental problems, such as acid rain, photochemical smog, and ozone



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depletion. The temperatures in gas engines or in the combustion of CBM in air are much higher (as high as 1600 °C) than that in SOFCs (700–900 °C), which markedly promote the formation of NO_x from the reaction of N₂ with O₂.⁸ In addition, SOFCs offer a modularity suitable for distributed power production with the highest efficiency at any load level. By contrast, gas turbines normally exhibit high efficiency only at high loads. Therefore, SOFCs operating on CBM promise to efficiently generate power for on-site use with minimized environmental impact. However, until now, few literature is available on the direct conversion of low-concentration oxygen-bearing CBM via SOFCs.

The primary challenge for conventional SOFCs with nickelbased cermet anodes operating on hydrocarbons is the coke formation over the anode, which consequently causes the rapid deterioration of cell performance.^{8,9} To solve this problem, several strategies have been developed to increase the coking resistance of the anodes.^{8,12} First, the Ni-free cermets or oxidebased anodes, such as Cu-based anodes and perovskite-type oxides, have been developed as anodes in recent years. However, their practical use is restricted, because of the newly emerging problems, such as low electrocatalytic activity, poor electrical conductivity, and bad chemical compatibility with other cell components. Meanwhile, the efforts to increase the coking resistance of Ni-based cermet anodes have never waned.^{9,16} The application of a catalyst layer with high catalytic activity for the reforming or partial oxidation of methane over the anode has been proven to be effective in coking resistance and performance improvement.¹⁷⁻²³ For example, LiLaNi-Al₂O₃/Cu, a cost-effective catalyst was developed for anode catalyst layers with high methane-reforming activity, good coking resistance, high electronic conductivity, and excellent thermomechanical compatibility with Ni-based anodes.²⁴⁻²⁶ Herein, we adopted this LiLaNi-Al₂O₃/Cu anode catalyst layer and extended its application to the conversion of oxygenbearing CBM in SOFCs. Another strategy is the addition of oxygen-containing gases, such as steam, CO₂, O₂, or air, into the fuel gas to increase the oxygen-to-carbon ratio and thereby avoid the coke formation thermodynamically.²⁷⁻³² It was reported that even the dilution of methane fuel with inert gases could cause a significant change in the anode reaction mechanism, resulting in a coking resistance effect.^{30,33,34} The above information suggests that there is great potential to take advantage of the diluent components, both active O2 and inert N₂, in low-concentration CBM for suppressing coke formation. In addition, the performance of SOFCs can be improved by optimizing the anode microstructure and the operating conditions.34-37

In the present work, the direct conversion of 30 vol % CBM to electricity via SOFCs with Ni-YSZ anodes was studied. The results indicate that the POM reaction of 30 vol % CBM plays an important role in improving the cell performance by supplying highly active gaseous fuels (H_2 and CO) and suppressing coking formation on the anodes. The operational stability was significantly improved more than 40-fold by integrating a LiLaNi–Al₂O₃/Cu catalyst layer over the anode, which greatly promoted the POM of 30 vol % CBM. These results suggest that the conversion of 30 vol % CBM via SOFCs is a promising way to utilize this abundant resource cleanly and efficiently.

2. EXPERIMENTAL SECTION

2.1. Fuel Composition. Table 1 lists the composition of the initial CBM sample obtained from the Shanxi Lanyan Coal-bed Methane

Table 1. Composition of the Initial Coal-Bed Methane(CBM) Sample

composition content (vol %)		
CH_4	91.4	
N_2	6.2	
O ₂	1.6	
CO ₂	0.6	
C_2	0.2	

Group Co., Ltd. (Jincheng, China). The 30 vol % CBM model sample was a mixture of the initial CBM sample with air, and its final methane content was 30 vol %.

2.2. Cell Fabrication. SOFCs used in this work were sandwichstructured cells with a $(Y_2O_3)_{0.1}(ZrO_2)_{0.9}$ (YSZ) thin-film electrolyte, a Ni-YSZ anode support, and a La_{0.8}Sr_{0.2}MnO₃ (LSM)-YSZ porous cathode, which were fabricated using a modified procedure.¹ Commercial NiO and YSZ powers were used as the anode materials, which were purchased from Chengdu Shudu Corporation, China and Tosoh, Japan, respectively. LSM powders were prepared by a combined EDTA-citrate complexing sol-gel technique.³⁶ The powders of NiO, YSZ, and polyvinyl butyral (PVB), in a weight ratio of 60:40:7, were mixed in ethanol by high-energy ball milling. This mixture was subsequently dried and ground manually under an infrared lamp. The composite anode powder with sizes of <150 μm was pressed to form a substrate in a stainless steel die. Then, pure YSZ powders were co-pressed onto the substrate to form a bilayer pellet, which was subsequently sintered at 1400 °C in air for 5 h. To deposit the cathode layer, the homemade LSM and commercial YSZ powders in a weight ratio of 7:3 were first dispersed in a mixture of glycerol, ethylene glycol, and isopropyl alcohol to form a colloidal suspension by high-energy ball milling. The cathode with a geometric surface area of 0.48 cm² was then fabricated by spray deposition of the colloidal suspension onto the dense YSZ electrolyte. The cathode was then sintered at 1100 °C in stagnant air for 2 h.

2.3. Catalyst Synthesis and Anode Catalyst Layer Preparation. The LiLaNi–Al₂O₃ catalyst, composed of Li₂O, La₂O₃, NiO, and balanced Al₂O₃ in a weight ratio of 1:5:30:64, was synthesized via a glycine nitrite process.²³ The composite catalyst, LiLaNi–Al₂O₃/Cu, was prepared by mechanically mixing of the LiLaNi–Al₂O₃ catalyst and copper in a weight ratio of 1:1 via manual grinding. Note that the source of copper was copper oxide (Aladdin Industrial Corporation, China). After mixing, the catalyst precursor was further calcined at 850 °C in static air for 5 h. To prepare the anode catalyst layer, the LiLaNi–Al₂O₃/Cu powder was first prepared into a colloidal suspension by dispersing it into a mixed solution of glycerol, ethylene glycol, and isopropyl alcohol by high-energy ball milling. The colloidal suspension was then deposited onto the anode surface by the spray deposition technique. The cell was further sintered at 850 °C in stagnant air for 2 h.

2.4. Characterizations. 2.4.1. Phase Structure of the Composite Catalyst. The phase structure of the composite catalyst was examined using a SmartLab X-ray diffractometer (Rigaku, Tokyo, Japan). The sample was packed into the rectangular cavity of a vitreous sample holder and scanned in a step-scan mode (0.02° per step) over a 2θ range from 10° to 90° (40 kV, 200 mA, Cu K radiation, $\lambda = 0.1541$ nm).

2.4.2. Coke Resistance of the Composite Catalyst. An oxygen temperature-programmed oxidation (O_2 -TPO) process was carried out to examine the coke resistance property of the composite catalyst, LiLaNi-Al₂O₃/Cu. First, carbon was deposited on the catalyst with ~0.2 g positioned in a quartz-tube reactor under an atmosphere of CBM or 30 vol % CBM at a flow rate of 40 mL min⁻¹ at 800 °C for 5 min. Then, under the protection of a helium atmosphere, the reactor was cooled to room temperature. Second, ~0.02 g of the catalyst with

deposited carbon were transferred into a U-type quartz reactor, where the catalyst were first purged by pure oxygen at a flow rate of 20 mL min⁻¹ through the top of the reactor at room temperature for 30 min, then the reactor was heated to 800 °C at a rate of 10 °C min⁻¹ and carbon deposited on the catalyst surface was gradually oxidized into CO₂. The CO₂ concentration of the effluent gas was monitored by a mass spectrometer (Hiden HPR-20) connected to the reactor. The laser Raman spectra of the Ni-YSZ anode material and LiLaNi-Al₂O₃/ Cu catalyst after the treatment at 800 °C under the 30 vol % CBM atmosphere for 1 and 10 h, respectively, were obtained in a LabRAM HR800 Raman spectrometer (Jobin Yvon, France) using the green line of an argon laser ($\lambda = 514.53$ nm) as the excitation source.

2.4.3. Performance Evaluation of the Cell Using CBM Fuel. Figure 1 shows the schematic of a single-cell test setup. The anode side of the



Figure 1. Schematic of the fuel cell test setup and the schematic structure of the SOFC (top).

cell was set onto the end face of a quartz/alumina tube and was sealed by silver paste. The cathode side of the cell exposed to ambient air. The test of electrochemical performances of the cell was performed using an Iviumstat electrochemical analyzer (Ivium Technologies B.V., The Netherlands). Electrochemical impedance spectra (EIS) from 0.1 Hz to 100 kHz were recorded with an alternate current signal amplitude of 10 mV under open-circuit conditions. The polarization curves of the cells were measured using a four-terminal mode. The anode was first reduced in H_2 with a flow rate of 40 mL min⁻¹ at 700 °C for at least 1 h. The anode chamber was purged by argon at a flow rate of 100 mL min⁻¹ for at least 30 min whenever the fuel supply was switched from one fuel to the other by a gas distribution device. The flow rates of hydrogen, CBM and 30 vol % CBM were maintained at 80, 40, and 40 mL min⁻¹, respectively. Ambient air was used as the oxidant during the entire test process. The cross-sectional morphology of the fuel cell was examined using an environmental scanning electron microscopy (ESEM) system (FEI, Model Quanta-200). The typical cell microstructure is shown in Figure 2a.

3. RESULTS AND DISCUSSION

3.1. Performance Comparison of the Fuel Cells Fed with CBM and 30 vol % CBM. Figure 2b shows the typical current–voltage (I-V) and current–power (I-P) characteristics of the fuel cell operating on hydrogen at various temperatures. This benchmark test aimed to check the reliability of cells used in this work. The OCV values for hydrogen fuel were 1.103, 1.096, and 1.087 V at 800, 825, and 850 °C, respectively, confirming that the electrolyte film was sufficiently dense and the cell was sealed tightly.³⁷

Figures 3a and 3b show the I-V and I-P curves of cells fed with CBM and 30 vol % CBM, respectively. The peak power densities (PPDs) for 30 vol % CBM were always higher than those for CBM at the corresponding temperature. The comparison of polarization cures for these two fuels at 850 °C is shown in Figure 3c. In the low-current-density range, the activated polarization of 30 vol % CBM was lower than that of CBM. The voltage drops (ΔV), which are defined herein as the value of the open-circuit voltage (OCV) minus the corresponding terminal voltage at a certain current density, which were 0.169 and 0.318 V for 30 vol % CBM and CBM at 200 mA cm⁻¹, respectively. In the high current density range, the limiting current density for these two fuels were almost identical (\sim 2900 mA cm⁻²), suggesting that 30 vol % CBM was able to support almost the same limiting current density as CBM did under the same conditions. Those data indicate that



Figure 2. (a) Typical SEM image of the cell microstructure, and (b) current-voltage (I-V) and current-power (I-P) curves of the cell operating on hydrogen.



Figure 3. I-V and I-P curves of the fuel cells fed with (a) CBM, and (b) 30 vol % CBM at various temperatures. The comparison of (c) the I-V curves at 850 °C, and (d) the open-circuit voltages (OCVs) at various temperatures.

30 vol % CBM might be more suitable as a fuel for SOFCs than CBM.

OCV values versus temperature for hydrogen, CBM and 30 vol % CBM from the test results are plotted in Figure 3d. The OCV values for both CBM and 30 vol % CBM increased linearly with increasing temperature, showing an opposite trend to that for hydrogen. These features agreed well with prior results and theoretical expectations and provide a clue to understand the anode reactions.^{34,38,39}

$$CH_4 \leftrightarrow C + 2H_2$$
 (R1)

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2$$
 (R2)

$$C + O^{2-} \rightarrow CO + 2e^{-} \tag{R3}$$

$$CH_4 + O^{2-} \rightarrow CO + 2H_2 + 2e^-$$
(R4)

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$
(R5)

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \tag{R6}$$

$$CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$$
 (R7)

Reactions R1, R4, and R7 are direct conversion channels for methane at the anode. The partial electrochemical oxidation of carbon (reaction R3) or methane (reaction R4) is responsible for the linear plot of OCV versus temperature with the largest positive slope.³⁸ In addition, these reactions generally result in higher OCV values (>1.2 V at 800 °C for dry methane). The conversion for 30 vol % CBM was more complex because multiple anode reactions occurred and intercoupled, and the equilibrium composition determined the OCV values. Reaction R1 may compete with reaction R2, and reactions R3–R7 could occur simultaneously at the Ni-based anode. Note that reaction R2 showed a significant impact on the OCV values of 30 vol % CBM, which were substantially lower than those of CBM. Briefly, Figure 3d indicates that the POM occurred in the anode chamber for 30 vol % CBM, but it was not the dominant reaction.

Generally, the *I*–*V* curves of SOFCs reflect the overall cell performance by convoluting variations in all the cell components. However, EIS measurements can isolate and associate specific frequency responses to certain electrode processes and provide detailed information on cell operational behavior. The low-frequency (LF, $10^{-1}-10^2$ Hz) responses are normally assigned to the gas diffusion process in porous anodes.⁴² The medium-frequency (MF, 10^2-10^4 Hz) responses are associated with the impedance of the electron-transfer and ion-transfer processes occurring at the current-collector/electrode and electrode/electrolyte interfaces, respectively.⁴¹ The response centered at 10^2-10^3 Hz arising from charge-transfer processes has been associated with an anode electrochemical process.^{40,42} The high-frequency (HF, >10⁴ Hz) response is assigned to the electrolyte resistance.



Figure 4. continued



Figure 4. Electrochemical impedance spectra (EIS) of the cells fed with (a) H_{22} , (c) CBM, (e) 30 vol % CBM at various temperatures, and (g) the comparison of them at 850 °C. The impedance difference spectra (IDS) of the EIS at 800 °C minus those at 850 °C for the cells fed with (b) H_{22} , (d) CBM, (f) 30 vol % CBM, and (h) the IDS of the cells fed with CBM versus those with 30 vol % CBM at 850 °C.

Figures 4a, 4c, and 4e show the Nyquist plots of EIS data collected from the fuel cells operating on various fuels at various temperatures. The polarization resistance (R_p) values of the fuel cells operating on various fuels all decreased significantly with increasing temperature. In particular, the R_p values for CBM, denoted as R_p (CBM), were always the largest ones at each temperature, and the following approximate relationship exists: R_p (CBM) $\approx 2.5 \times R_p$ (30 vol % CBM) $\approx 5 \times R_p$ (H₂). The case at 850 °C is presented in Figure 4g for direct comparison.

To further understand the factors that dominate the $R_{\rm p}$ values of SOFCs, we introduce the impedance difference spectra (IDS) concept, which is defined as the difference of resistance (Re Z) or capacitance (Im Z) values of the two sets of EIS data at corresponding frequencies.²² By IDS, the resistance or capacitance responses from the identical factors are counterbalanced, and the factors that lead to the difference are prominent. The IDS can be analyzed by the resistance gradients (R) in various frequency ranges, namely, R(LF), R(MF), and R(HF). The resistance gradient R, in units of Ω cm^2 is defined as the difference value of the resistance (Re Z) value at the lowest frequency minus that at the highest frequency of a certain frequency range. The objective by introducing this concept is to describe the increase of the resistance in certain frequency range (e.g., the low-frequency range), which is closely related to certain polarization behavior (e.g., the concentration polarization). Table 2 lists the R data extracted from Figure 4. Note that, in the present work, the LF

Table 2. Resistance Gradients (*R*) at Low-and Medium-Frequency Ranges in Figure 2

	Resistance Gradient, R (Ω cm ²), in Various Frequency Ranges	
case	R(LF)	R(MF)
H ₂ , 800 °C vs H ₂ , 850 °C	0.0907	0.0821
CBM, 800 °C vs CBM, 850 °C	1.0330	0.3876
30% CBM, 800 °C vs 30% CBM, 850 °C	0.0589	0.2225
CBM vs 30% CBM, 850 °C	1.3055	0.0649

range is from 10^{-1} Hz to 10 Hz, the MF range is from 10 Hz to 10^{3} Hz, and the HF is from $10^{3}-10^{6}$ Hz.

Combined with the data in Table 2, further analysis of the EIS data in Figure 4 is given below. Figure 4b shows the IDS of the cells using hydrogen fuel at 800 °C versus that at 850 °C, which provides baseline information on the effect of temperature increase on the polarization resistance from the gas diffusion (i.e., $R(LF)-H_2$) and charge-transfer process or electrode electrochemical process (i.e., $R(MF)-H_2$). Obviously, they are very much closer to each other. Figure 4d presents the IDS of the cells using CBM fuel at 800 °C versus that at 850 °C. As mentioned above, the EIS response in the LF range normally arises from the gas diffusion process in porous anodes, the R(LF)-CBM value is significantly larger than that of R(MF)-CBM, suggesting that the diffusion process of CBM makes the primary contribution to the cell polarization. In contrast, the IDS of the cells using 30 vol % CBM fuel at 800 °C versus that at 850 °C in Figure 4f shows that the chargetransfer process may dominate the cell polarization, because the R(MF)-(30 vol % CBM) value is 3.8 times that of the R(LF)-(LC-CBM). Figure 4h shows the IDS of the cells using CBM versus that using 30 vol % CBM at 850 °C. The result is similar that in Figure 4d, indicating that the diffusion polarization of CBM may be the most important polarization factor to CBM.

A series of evidence indicated that the adoption of an anode catalyst layer was able to efficiently suppress carbon deposition on nickel cermet anodes and to increase the operational stability and performance of hydrocarbon-fueled SOFCs.¹⁴⁻²² Among the catalysts developed by our group, LiLaNi-Al₂O₃/ Cu displayed sufficient catalytic activity and high stability for the partial oxidation, steam reforming, and CO₂ reforming of methane.^{21–23} We found that the catalytic activity of Ni–Al₂O₃ was significantly greater than that of Ni-based cermet anodes and was comparable to that of Ru-CeO2.²¹ The coking resistance and surface electrical conductivity of the Ni-Al₂O₃ catalyst were substantially enhanced by the modification of Li₂O and La₂O₃ and the introduction of copper, respectively.^{22,23} Figure 5 presents the X-ray diffraction (XRD) pattern of the LiLaNi-Al₂O₃/Cu catalyst, which is consistent with that reported in the literature, after calcining at 850 °C in air for 5 h. $^{2\$}$ The detected Al_2O_3 and $NiAl_2O_4$ crystalline phases



Figure 5. X-ray diffraction (XRD) pattern of the LiLaNi–Al $_2O_3/Cu$ catalyst after calcination at 850 °C.

illustrate that NiO had strongly interacted with Al_2O_3 . No detection of the peaks of La_2O_3 and Li_2O reflects that they were thoroughly scattered in the sample. In addition, the observed

 $CuAl_2O_4$ spinel phase suggests that copper partially replaced the nickel in NiAl₂O₄, which led to the formation of NiO phases. Herein, we developed a fuel cell design with the LiLaNi–Al₂O₃/Cu anode catalyst layer for using 30 vol % CBM fuel.

Figure 6a presents the comparison of operational stability of the cells fueled with CBM and 30 vol % CBM. For the cell using CBM fuel, the operation with a terminal voltage of 0.72 \pm 0.02 V maintained for \sim 43 min, after which the voltage sharply decreased to zero within 4 min. In the first 43 min, the voltage increased slightly, suggesting that carbon deposited and accumulated on the anode. Meanwhile, the high voltage indicates that a carbon electrochemical oxidation occurred simultaneously.^{43,44} However, excessive carbon deposition on the anode was fatal to the cell, which hindered the pores of anodes, destroyed the cell's integrity (inset in Figure 6a), and eventually resulted in rapid degradation in cell's performance.⁴⁵ By contrast, the operation of cells with 30 vol % CBM persisted for \sim 270 min. Within the first 120 min, the terminal voltage kept at 0.74 \pm 0.04 V and then gradually decreased to zero. A series of evidence has proved that the deployment of an anode catalyst layer was able to efficiently suppress carbon deposition on the nickel cermet anodes of hydrocarbon-fueled



Figure 6. Stability tests of the cells (a) without the catalyst layer fed with CBM and 30 vol % CBM and (b) with the catalyst layer using 30 vol % CBM, at a current density of 370 mA cm⁻² and 800 °C. The insets in panels (a) and (b) are digital photographs of the cells after the stability test. (c) O_2 -TPO profiles of the catalyst after treatment with CBM and 30 vol % CBM for 5 min at 800 °C, respectively. (d) Raman spectra of the Ni-YSZ anode material and LiLaNi–Al₂O₃/Cu catalyst after the treatment in 30 vol % CBM at 800 °C for 1 and 10 h, respectively.

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SOFCs.^{17–23} Our previous work showed that the LiLaNi– Al₂O₃/Cu catalyst displayed sufficient catalytic activity and high stability for the partial oxidation, steam reforming, and CO₂ reforming of methane.^{24–26} The coking resistance and surface electrical conductivity of the Ni–Al₂O₃ catalyst were substantially enhanced by the modification of Li₂O and La₂O₃ and the introduction of copper, respectively. Figure 6b presents the stability test for the cell with the LiLaNi–Al₂O₃/ Cu layer operating on 30 vol % CBM. The terminal voltage (~0.75 V) and power output (~280 mW cm⁻²) of the cell remained almost constant during the 120 h test period and the cell without any crack (inset in Figure 6b). The duration was significantly longer than that of the cell without the catalyst layer (2.8 h with a voltage of >0.6 V (Figure 6a)).

For better understanding of the degradation of the cell performance and the coking-resistance property of the catalyst layer, O2-TPO and Raman analyses were performed. Figure 6c shows the result of O₂-TPO analysis of the LiLaNi-Al₂O₃/Cu catalyst of exposure to 30 vol % CBM or CBM. The areas of CO_2 peaks for CBM and 30 vol % CBM are 1.01 × 10⁻⁶ and 5.94×10^{-7} Torr min, respectively, which are directly proportional to the amount of carbon deposited on the catalyst. By applying pure SrCO₃ as an external standard, the amount of the deposited carbon can be quantitatively determined.²⁷ In fact, the rates of carbon deposition are 2.51 \times 10⁻⁴ and 4.27 \times 10⁻⁴ mol (g min)⁻¹ for exposure to 30 vol % CBM and CBM, respectively. The former is obviously slower than the latter. Raman spectroscopy analysis is a powerful tool to investigate the structure of deposited carbon and to examine the coking or coking-resistance property of materials. Figure 6d shows the Raman spectra of the Ni-YSZ anode material and LiLaNi-Al2O3/Cu catalyst of exposure to 30 vol% CBM atmosphere at 800 °C for 1 and 10 h, respectively. The two intense bands at ~1350 cm⁻¹ (the D-band) and ~1580 cm⁻¹ (the G-band) are assigned to the structural disorder of carbon and the in-plane vibrations of carbon atoms in hexagonal sheets, respectively.¹⁵ The degree of graphitization of the deposited carbon is related to the integrated intensity ratio of these two bands in the form of I(D)/I(G), and the ratio values should decrease as the degree of graphitization of the carbon increases.¹⁵ The I(D)/I(G) values of the carbon deposited on the LiLaNi-Al₂O₃/Cu catalyst and the Ni-YSZ anode material are 1.74 and 0.69, respectively, which indicates that the degree of graphitization of the carbon deposited on the Ni-YSZ is higher than that on the LiLaNi-Al₂O₃/Cu catalyst. Therefore, the coking resistance property of the LiLaNi-Al₂O₃/Cu catalyst is higher than that of the Ni-YSZ material. The following factors may play an important role in mitigating carbon deposition, leading to better operational stability for 30 vol % CBM: (i) the presence of ~15 vol % O_2 content, which intrinsically induced the POM, and the POM was further promoted by the LiLaNi-Al₂O₃/Cu catalyst, (ii) the presence of ~55 vol % N_2 content, which greatly diluted the CH_4 concentration, and could block the nickel active sites in the anode by coadsorbing and interfere with the process of concentrated methane being adsorbed at many adjacent sites on nickel to produce carbon layers (graphitization) by separating the carbon atoms, allowing oxygen to diffuse from the zirconia/nickel boundary to give oxidation.³⁴

Figure 7 summarizes the results of the stability tests. The lifetime of the cell without the catalyst layer operating on CBM was approximately one-fifth of that operating on 30 vol% CBM. For the cell with the catalyst layer fed with 30 vol%





Figure 7. Comparison of the stability of the cells operating under various conditions. The inset is a schematic diagram of the conversion process of CH_4-O_2 gas mixtures in the cell with a catalyst layer.

CBM under constant current, the operation was quite stable during the 120-h test, which was ~40-fold longer than that of the cell without the catalyst layer. The results indicate that LiLaNi-Al₂O₃/Cu is a highly coking-resistant catalyst suitable for use as the functional layer of the cell operating on oxygencontaining CBM. The inset of Figure 7 presents the schematic of chemical and electrochemical reactions occurring in the cell with an anode catalyst layer. Once the CH_4 and O_2 in 30 vol % CBM reached the catalyst layer, the partial oxidation reaction of CH_4 (R2) was catalyzed and produced H_2 and CO, which further diffused into the anode and arrived at the three-phase boundary (TPB) where they met oxygen anions and were electrochemically oxidized to H₂O and CO₂ with electricity generation. The electrochemical activities of H₂ and CO are higher than that of methane, the cell performance was thus improved.⁹ Therefore, the modification of the anode surface by the catalyst layer is an effective strategy to improve the performance of SOFCs operating on low-concentration oxygen-containing CBM.

3.2. Performance of the Fuel Cells with Anode Catalyst Layer Operating on 30 vol % CBM. Figure 8a shows the I-V and I-P curves of the cells with LiLaNi-Al₂O₂/ Cu catalyst layer fed with 30 vol % CBM at various temperatures. The PPD achieved $\sim 1068 \text{ mW cm}^{-2}$ at 850 $^{\circ}$ C, which is only modestly lower (~15%) than that from the cell based on hydrogen fuel. The average PPD values were \sim 1.34 and 1.61 times greater than those of the cells without a catalyst layer, using 30 vol % CBM and CBM fuel, respectively (see Figures 3a and 3b). In brief, the PPD values ranked in the order of H₂ > (30 vol % CBM + catalyst layer) > 30 vol % CBM > CBM, which is very consistent with the order of the polarization resistance (R_p) values, $H_2 < (30 \text{ vol }\% \text{ CBM} +$ catalyst layer) < 30 vol % CBM < CBM, as shown in Figures 8b, 4a, 4c, and 4e. Figure 8c shows the IDS of the cells with catalyst layer using 30 vol % CBM fuel at 800 °C, versus that observed at 850 °C. The R(LF) and R(MF) values are 0.074 and 0.19 Ω cm², respectively, suggesting that the chargetransfer process or anode electrochemical process might dominate the polarization resistance.

For conciseness and clarity, the cells with and without a catalyst layer using 30 vol % CBM fuel at 850 °C are referenced as cases A and B, respectively. As shown in Figure 8d, the activated polarization for case A in the low-current-density



Figure 8. (a) I-V and I-P curves and (b) EIS of the cells with the catalyst layer fed with 30 vol % CBM at various temperatures, and (c) EIS difference spectra of the values extracted from panel (b). Also shown is a comparison of (d) I-V curves and (e) EIS of the cells with and without the catalyst layers fed with 30 vol % CBM at 850 °C, and (f) EIS difference spectra of the values extracted from panel (e).

range was less than that for case B, suggesting that more H₂ and CO might be produced from the methane partial oxidation promoted by the catalyst layer. Because H₂ and CO have a higher electrochemical reactivity than methane, the replacement of methane with H₂ and CO can decrease the activated polarization.^{9,46} This is further supported by the EIS data in Figure 8e: the polarization resistance of case A (0.68 Ω) was significantly less than that of case B (1.23 Ω). In addition, the ohmic resistance of case A (0.06 Ω) was less than that of case B (0.12 Ω), indicating that the electronic conductivity of the

catalyst layer was good enough for the current collection and that the heat produced from the methane partial oxidation might increase the real temperature of the anode to a level higher than the measured value of the furnace, which would result in a decrease of ohm resistance of the electrolyte. Figure 8f shows the IDS of these two cases. The R(LF) and R(MF) values are 0.084 and 0.23 Ω cm², respectively, suggesting that the charge-transfer process or anode electrochemical process might dominate the polarization resistance.

3.3. Effect of Increasing Temperature on the Increase of PPD: Coupling Effect of Anode Reactions. The PPD values of the cells operated under various conditions ranked in the order of PPD-H₂ > PPD-(30 vol % CBM + catalyst) > PPD-(30 vol % CBM) > PPD-CBM, at the corresponding temperatures (Figure 9a). With regard to using 30 vol % CBM



Figure 9. (a) Comparison of the peak power densities of the cells operating under various conditions; the term "30 vol % CBM + catalyst" indicates the cell with the anode catalyst layer using 30 vol % CBM. (b) Comparison of the increasing ranges of normalized peak power densities (NPPD).

fuel, the average PPD value of the cells with the catalyst layer at 800, 825, and 850 $^{\circ}$ C was ~1.4 times that of the cells without the catalyst layer. Note that, among the above four cases, the cell without a catalyst layer using CBM fuel exhibited the maximum increase of PPD with increasing temperature; however, the cell with a catalyst layer using 30 vol % CBM exhibited the minimum. This feature is presented in detail in Figure 9b. Herein, the normalized peak power density (NPPD) is defined as follows:

$$NPPD = \frac{PPD_{T}}{PPD_{800}}$$
(8)

where PPD_{800} represents the PPD value at 800 °C, and PPD_T represents the PPD value at 800, 825, or 850 °C. The increasing range of the normalized peak power density (NPPD) is defined as follows:

$$\Delta NPPD = \Delta NPPD-1 + \Delta NPPD-2 \tag{9}$$

$$\Delta \text{NPPD-1} = \text{NPPD}_{825} - \text{NPPD}_{800} \tag{10}$$

$$\Delta \text{NPPD-2} = \text{NPPD}_{850} - \text{NPPD}_{825} \tag{11}$$

where NPPD₈₅₀, NPPD₈₂₅, and NPPD₈₀₀ represent the NPPD values at 850, 825, and 800 $^{\circ}$ C, respectively.

Based on the anode reaction mechanism, the influence of methane's chemical reactions over the anode on NPPD of the cells operated under various conditions was discussed below. For SOFCs fueled with methane-based fuels, the anode side involves up to 14 possible electrochemical and chemical reactions, which constitute a complex coupling system containing a maximum of six components with thermodynamic stability: the deposited carbon, CO, H₂, CO₂, H₂O, and some residual CH₄.^{9,46} In contrast, when using H₂ fuel, only the electrochemical oxidation of H₂ occurs at the anode; there is not any chemical reaction occurrence, so there is no coupling effect between the chemical reaction(s) with the electrochemical reaction(s). Therefore, the Δ NPPD of cells using H₂, $\Delta NPPD-H_2 = (\Delta NPPD-1 + \Delta NPPD-2)-H_2$, is taken as the coupling-free benchmark. The other Δ NPPD terms, which are greater or less than $\Delta NPPD-H_2$, indicate the existence of a positive or negative coupling effect. As shown in Figure 9b, the Δ NPPD values of various fuels with increasing temperature are ranked in the order of Δ NPPD-CBM > Δ NPPD-(30 vol % $(CBM) > \Delta NPPD-H_2 > \Delta NPPD-(30 \text{ vol }\% CBM + \text{ catalyst}),$ which could be understood as follows.

The methane decomposition that is decribed by reaction R1 is an endothermic reaction ($H_{298 \text{ K}} = +75 \text{ kJ mol}^{-1}$), which is the dominant chemical reaction for CBM at the Ni-based anode without a catalyst layer.⁴⁷ Increasing the temperature favors this reaction and leads to the increase of H₂ and solid carbon products, which is beneficial for the increase of PPD in a sense. With increasing temperature, the Δ NPPD-CBM reaches the maximum, reflecting a very strong positive coupling effect of reaction R1 with the electrochemical reactions. In contrast, the partial oxidation of methane (reaction R2) is an exothermic reaction ($H_{298 \text{ K}} = -36 \text{ kJ mol}^{-1}$), which might be the dominant chemical reaction for 30 vol % CBM at the anode with a catalyst layer.⁸ Increasing temperature is unfavorable to the reaction thermodynamically and leads to a decrease in the rate of increase of H₂ and CO production, which is not beneficial for the increase of PPD. Thus, with increasing temperature, the Δ NPPD-(30 vol % CBM + catalyst) reaches the minimum, suggesting a strong negative coupling effect of reaction R2 with the electrochemical reactions. For 30 vol % CBM at the anode without a catalyst layer, both reactions R1 and R2 can occur and compete with each other. Increasing the temperature is favorable for reaction R1 but not for reaction R2. The overall effect is beneficial to the increase of PPD to a certain extent. Therefore, with increasing temperature, $\Delta NPPD$ -(30 vol % CBM) > Δ NPPD-H₂, showing a certain positive coupling effect. In brief, these results reveal that the coupling effect of the cell using CBM fuel with increasing temperature is an important factor influencing the power output and should be taken into account for improving the cell performance.

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4. CONCLUSION

The feasibility of direct conversion of 30 vol % CBM via SOFCs was investigated in the present work. The fuel cell using 30 vol % CBM fuel showed a higher performance than that using high-concentration CBM (91 vol % CH₄) fuel, which suggests that the POM of 30 vol % CBM played a positive role on the cell performance. By integrating a LiLaNi-Al₂O₃/Cu catalyst layer over the anode, the POM of 30 vol % CBM was greatly promoted and the cell performance was improved significantly. A maximum power output of ~1068 mW cm⁻² was achieved at 850 °C for a cell with the catalyst layer operating on 30 vol % CBM fuel, which is only modestly lower than that from a cell based on hydrogen fuel. The cell operation was quite stable during the 120-h test, which was ~40-fold longer than that of the cell without a catalyst layer. Therefore, the strategy of direct conversion of low-concentration oxygenbearing CBM via SOFCs with an anode catalyst layer is a promising way to utilize this abundant resource efficiently and cleanly.

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE

CBM = coal-bed methane EIS = electrochemical impedance spectra GWP = global warming potential HF = high frequencyIDS = impedance difference spectra I-P = current-power density curveI-V = current-voltage curveLF = low frequency $LSM = La_{0.8}Sr_{0.2}MnO_3$ MF = middle frequency NPPD = normalized peak power density OCV = open-circuit voltage O_2 -TPO = oxygen temperature-programmed oxidation POM = partial oxidation of methane PPD = peak power density PVB = polyvinyl butyral R = resistance gradient

 $R_{\rm O}$ = ohmic resistance $R_{\rm P}$ = polarization resistance SOFC = solid oxide fuel cell TPB = triple phase boundary ΔV = voltage drop YSZ = yttrium-stabilized ZrO₂

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