Short communication

Application of a Cu–CeO$_2$/Ni–yttria-stabilized zirconia multi-layer anode for anode-supported Solid Oxide Fuel Cells operating on H$_2$–CO syngas fuels

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ABSTRACT

A Ni–yttria-stabilized zirconia (YSZ) anode and a Cu–CeO$_2$/Ni–YSZ multi-layer anode have been fabricated for use in anode-supported Solid Oxide Fuel Cells (SOFCs), and their performances and stabilities in H$_2$–CO syngas have been studied at 750 °C. A high CO content has been found to cause carbon deposition and crack formation in the Ni–YSZ anode after long-term operation, but the Cu–CeO$_2$ catalyst layer on the Ni–YSZ anode surface improves its stability in syngas with high CO content by facilitating the water gas shift reaction. The optimized single cell has run in syngas with a composition of 48.5%H$_2$–48.5%CO–3%H$_2$O for 460 h without obvious degradation of its performance, however, its performance decreases after 630 h due to carbon deposition in the anode functional layer and subsequent crack formation on the anode and electrolyte.
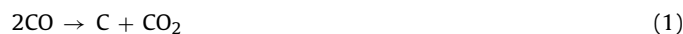
1. Introduction

The importance of replacing fossil fuels with sustainable and renewable energy sources in order to achieve a reduction in greenhouse gas emissions has been of great concern in recent years. Solid Oxide Fuel Cells are among the most attractive energy conversion devices because of their high efficiency, low pollution, and multi-fuel compatibility. The high operating temperature gives rise to excellent fuel flexibility. Not only hydrogen but also various kinds of hydrocarbon such as natural gas [1], biogas [2], alcohols [3,4] and coal-derived syngas [5] have been studied as fuels for SOFCs.

At the operating temperatures of SOFCs, hydrocarbon fuels may decompose in the gas-phase, react catalytically, or be reformed by steam in the anode compartment, leading predominantly to products of hydrogen (H$_2$) and carbon monoxide (CO), along with some other species depending on the initial feed. The steam gasification of coal can produce a stream that contains 30% H$_2$ and 60% CO [6], while biomass gasification may produce a mixture with 17% H$_2$ and 13% CO [7]. Direct utilization of these syngas streams as fuels for SOFCs not only increases the energy efficiency and reduces the operational cost of power generation, but also provides flexibility for carbon dioxide sequestration [8].

It is well known that Ni–YSZ cermet anodes can be directly used for hydrocarbon fuels only if excess steam is present to ensure

complete fuel reforming and to suppress carbon deposition [9]. For H$_2$–CO syngas, carbon formation occurs through reaction (1) (Boudouard reaction) and reaction (2) [10]. The addition of water steam to syngas can promote the water gas shift reaction (WGS, reaction (3)) to generate H$_2$, and the reformed CO$_2$ suppresses disproportionation [10]. However, high steam addition lowers the electrical efficiency of the system.

$$2CO \rightarrow C + CO_2 \tag{1}$$

$$CO + H_2 \rightarrow C + H_2O \tag{2}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{3}$$

How to improve the Ni–YSZ stability in syngas without introducing much steam is a major challenge for syngas utilization. In the present study, we have fabricated anode-supported SOFCs with Ni–YSZ and Cu–CeO$_2$/Ni–YSZ anodes and measured the performances of the cells in H$_2$–CO syngas fuels of different compositions. The Ni–YSZ anode stability and carbon deposition were monitored upon discharging in syngas with high CO content. A Cu–CeO$_2$ catalyst layer on the Ni–YSZ anode surface was found to suppress carbon formation and to improve its long-term stability in syngas. The optimized single cell operated in syngas with a composition of 48.5%H$_2$–48.5%CO–3%H$_2$O for 460 h with a stable power density output of around 280 mW cm^{-2}. However, carbon deposition in the anode functional layer and consequent performance degradation was finally observed after 630 h.

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2. Experimental

2.1. Fabrication of the single cells

A typical single cell used in the present work consists of a NiO-YSZ supported anode layer, a NiO-YSZ anode functional layer, a YSZ electrolyte and a LSM ($(La_{0.8}Sr_{0.2}) MnO_3$) cathode layer, which was fabricated by tape-casting and screen-printing technology. The anode-supported electrolyte composite membrane was fabricated by multi-layer tape casting and co-sintering, as has been typically employed by our group. Details of the process of its manufacture can be found elsewhere [11]. The sintering temperatures for the composite membrane and the cathode layer were 1450 °C and 1200 °C, respectively. Two single cells were fabricated by the aforementioned process, which are denoted herein as cell 1 and cell 2. For cell 2, a Ni–CeO2 interlayer was also fabricated on the Ni–YSZ surface in this way, as described in our previous work [12]. The effective area of each cell was 1.4 cm^2.

The catalyst powders of Cu–CeO2 composite oxides were prepared by the citric acid method as follows: An aqueous solution containing all required ions as metal nitrates ($Cu(NO_3)_2 \cdot 3H_2O$, $(NH_4)_2Ce(NO_3)_6 \cdot 6H_2O$) and citric acid ($C_6H_8O_7 \cdot H_2O$) were used as starting materials, and the catalyst calcination temperature was 800 °C. The catalyst powders with Cu/CeO2 weight ratio of 1:3 were fabricated in this way, which were then screen printed onto the anode surface of cell 2 and finally sintered at 1100 °C for 3 h. Except for the catalyst layer, cell 1 and cell 2 have the same parameters, which include a supported anode thickness of 700 µm, an electrolyte thickness of 20 µm, and a cathode thickness of 30 µm.

2.2. Characterization of single cell performance

SOFC tests were carried out with a single cell test setup, which was illustrated in our previous publication [4]. Pt meshes as current collectors and Au lead wires in a four-probe configuration were attached to the surfaces of the anode and cathode using Pt paste. The cathode side of the structure was then attached to an alumina tube and the edges were sealed using a glass ring. The anodes were fully reduced in H2 atmosphere for several hours prior to cell testing, and the electrochemical tests were carried out at 750 °C.

Mixtures of H2 and CO, with their compositions regulated by a set of mass-flow controllers were used as fuels, and oxygen was used as an oxidant. A humidity bottle was employed to achieve the desired water vapor partial pressure. The fuel and oxidant flow rates were both controlled at 30 mL min^{-1}. The current–voltage curves and electrochemical impedance spectra (EIS) were obtained using an Electrochemical Workstation (IM6e, ZAHNER). Impedance spectra of the electrochemical cells were recorded at open circuit voltage (OCV) over the frequency range from 100 kHz to 10 MHz with an excitation potential of 20 mV. The microstructure and morphology of the single cell structure were examined by scanning electron microscopy (SEM, JXA-8100, JEOL Co. Ltd., Japan).

3. Results and discussion

3.1. Performance characterization of the anodes in syngas

Fig. 1 shows the voltage and power density vs. current density curves measured at 750 °C for cell 1 (a) and cell 2 (b) in syngas, where the gas composition was varied between 97% H2 and ~48.5% H2. The OCV and the maximum power density of cell 1 are seen to exhibit a dependence on the syngas concentration. When the CO content was high, the cell performance was limited by high anodic concentration polarization and slower electrochemical oxidation of CO [13]. Although cell 2 showed lower activation loss due to the
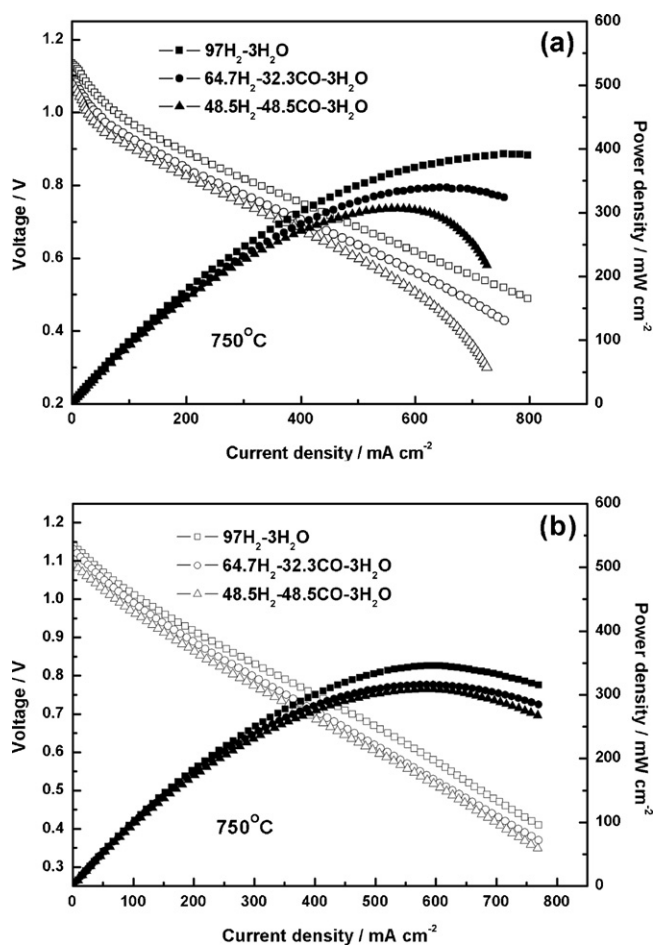

Fig. 1. Voltage (open) and power density (closed) vs. current density for cell 1 (a) and cell 2 (b) in syngas fuels with different compositions at 750 °C.

catalytic activity of the ceria in the Cu–CeO2 layer, it showed lower performance in hydrogen compared to cell 1 as a result of multi-layer structure of the anode and the increased ohmic resistance [12]. However, the cell performance in syngas with a H2:CO ratio of 1:1 was found to be very similar to that in H2, which is very different from what was found for cell 1. The Cu–CeO2 catalyst layer can improve the anode performance in syngas, especially when the CO content is high, by facilitating the WGS reaction before CO is introduced into the Ni–YSZ anode matrix. As CO has a slower gas diffusion rate and slower electrochemical rate than H2 [14], additional hydrogen produced by the WGS reaction improves the gas diffusion and electrochemical oxidation of the syngas fuel.
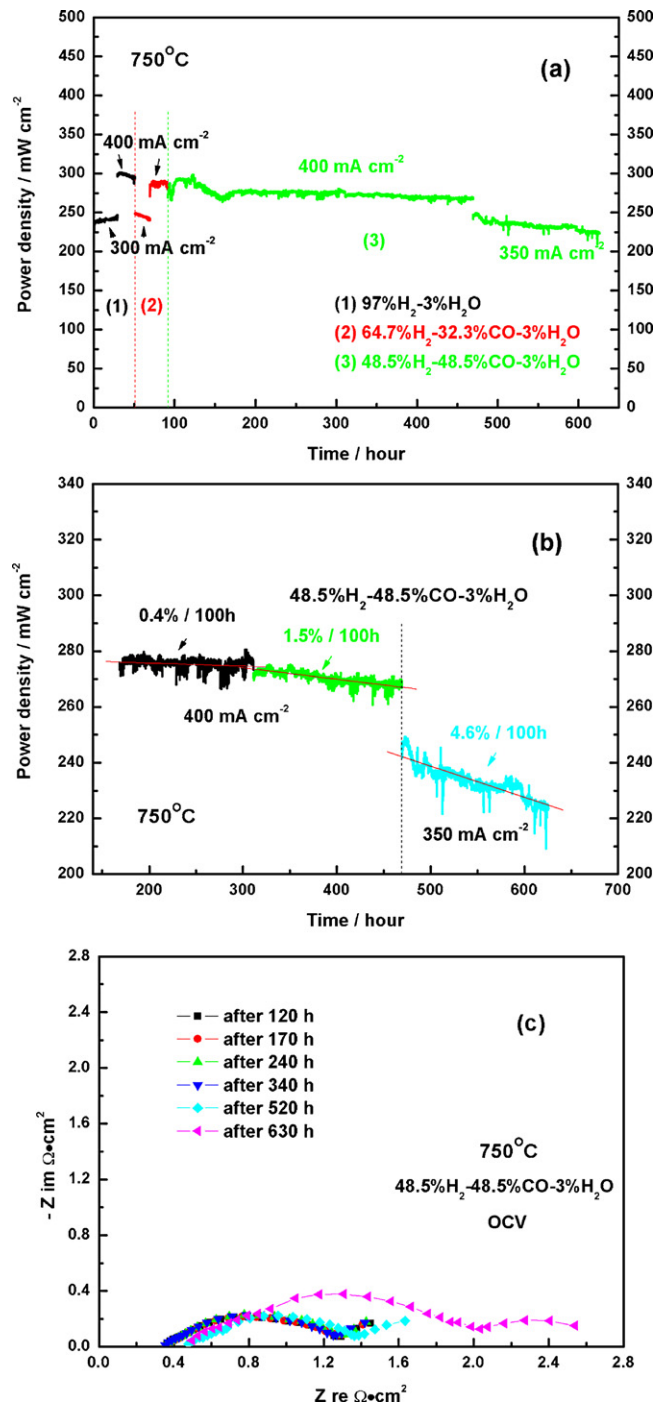
3.2. Long-term stability of the anodes in syngas

Fig. 2(a) shows curves of power density as a function of operation time for cell 1, obtained by discharging at a constant current density of 200 mA cm^{-2} in different syngas compositions at 750 °C. Although cell 1 displayed stable output in syngas for as long as ~320 h, some oscillations are observed in the curves after 200 h, which are probably due to the appearance of some micro-cracks in the anode as a result of carbon deposition. We found that carbon deposition from CO can lead to disintegration of the anode after operation, especially in its edge area, where there is little current density. The photographs in Fig. 2(b) and (c) illustrate the phenomenon of anode cracking, which may lead to some leakage of fuel gas and hence to decreases in the OCV and anode performance.
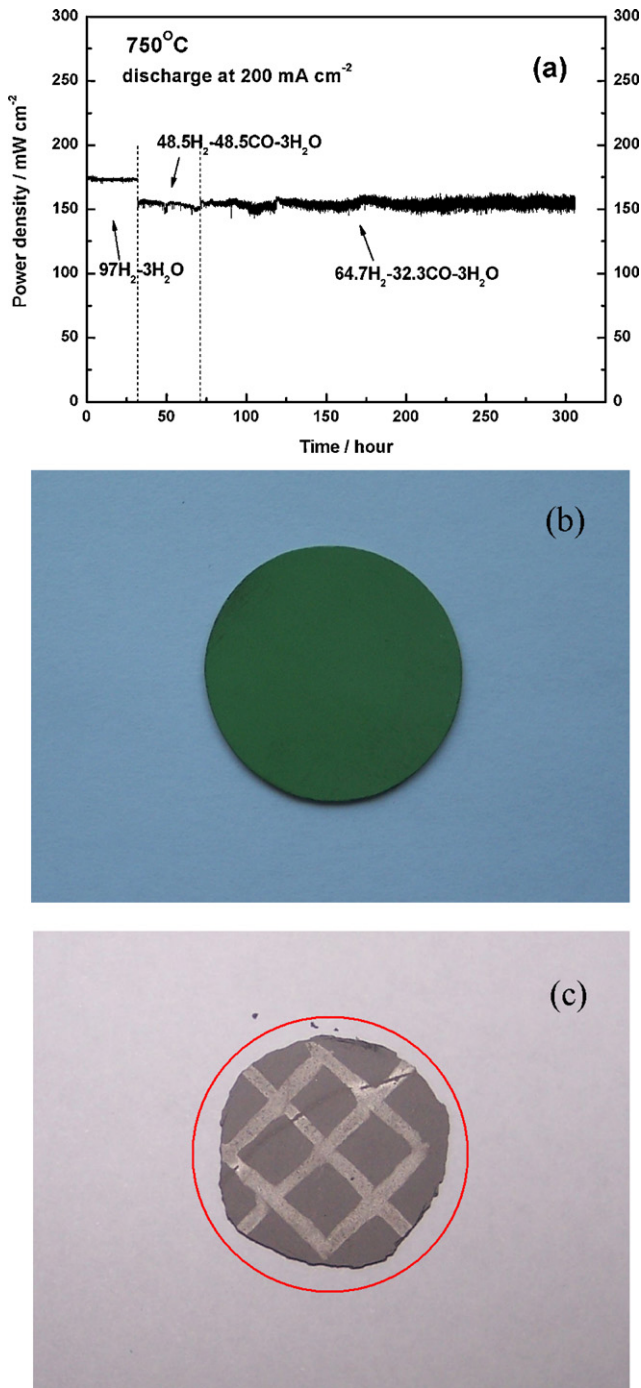
Fig. 2. Power density as a function of time for cell 1 (a) while discharging under constant current density at 750 °C and photographs of this cell before (b) and after (c) operation.


Fig. 3. Power density as a function of time for cell 2 (a, b) and impedance spectra under open circuit voltage (c) while operating in hydrogen and syngas at 750 °C.

Fig. 3(a) shows the stability of cell 2 running in syngas with composition of 48.5%H$_2$–48.5%CO–3%H$_2$O for an operation time of as long as 630 h. Although the current density was higher than that of cell 1, cell 2 showed better stability in syngas with higher CO content. We can see in Fig. 3(b) that there were three distinct stages for the performance degradation of cell 2. In the initial 300 h of operation in syngas, the degradation rate was less than 0.4% per 100 h, while from 300 h to 460 h, the degradation rate was 1.5% per 100 h. In the final 200 h of operation time, the degradation rate was as high as 4.6% even though the current density was reduced to 350 mA cm^{-2}. These results were accompanied by an increase in the

ohmic resistance or polarization resistance of the cell in impedance spectra, as shown in Fig. 3(c), and the increased polarization resistance seemed to lead to faster degradation.

CO can still make its way to the Ni–YSZ anode matrix, considering the thickness of the catalyst layer. Therefore, carbon formation is still a problem over longer operation times, which will cause irrevocable damage to the single cell. Fig. 4(a) demonstrates the carbon deposition phenomenon and its damage to the single cell. There was no obvious carbon deposition in the Cu–CeO$_2$ catalyst layer or the Ni–YSZ supported anode, as is evident from Fig. 4(b), and these two layers maintained a good interface combination. However, from Fig. 4(c) we can see that some short carbon fibres
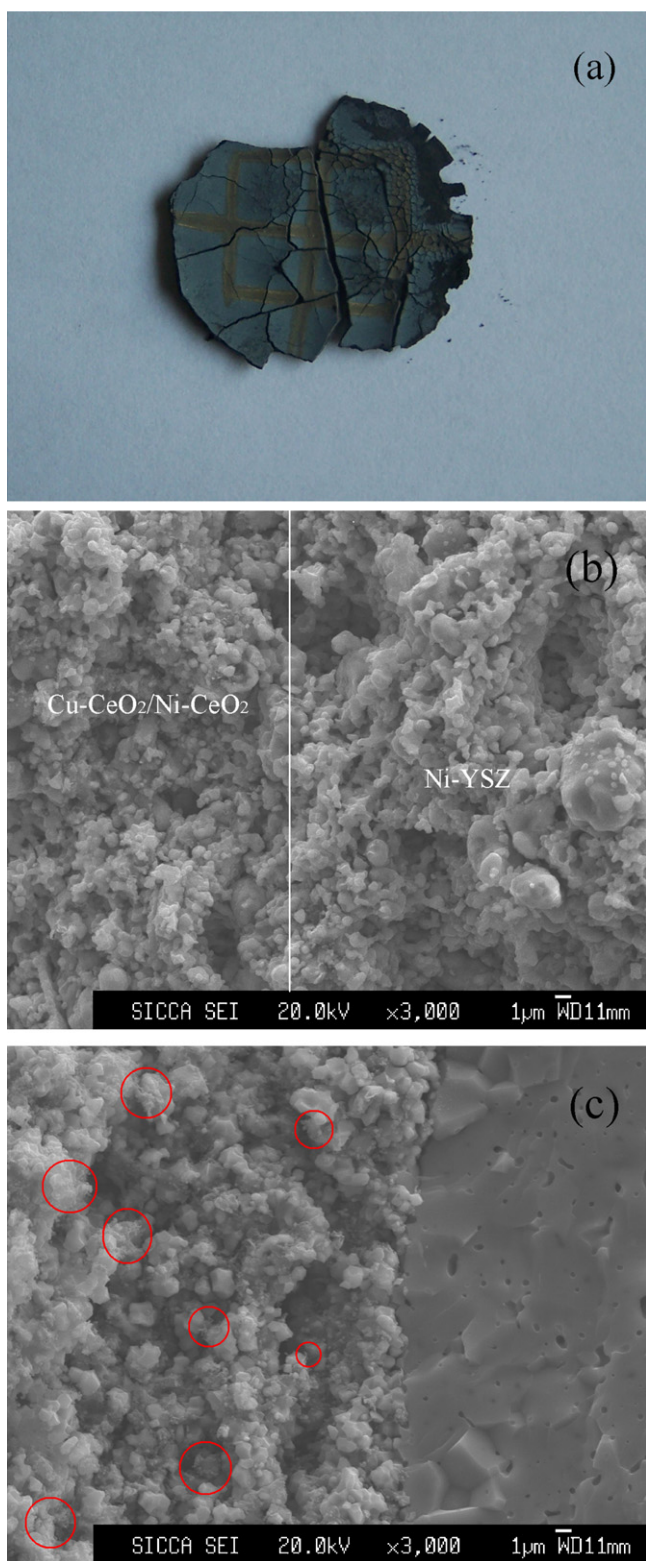
Fig. 4. Photograph (a) and cross-sectional SEM images (b, c) of cell 2 after operation in syngas longer than 630 h at 750 °C.

appeared in the anode functional layer and in the adjacent supported anode layer, which is close to the electrolyte and where the electrochemical reaction takes place. As the Cu–CeO_2 catalyst is screen printed on the anode surface, the CO that infiltrates the catalyst layer will undergo the WGS reaction and produce a distribution gradient in the anode direction. Therefore, carbon deposition is more likely to occur in the area close to the electrolyte. We have impregnated Cu–CeO_2 catalyst into the Ni–YSZ anode, whereupon the impregnated anode has shown better stability in syngas fuel [15]. Therefore, the combination of catalyst layer on anode surface and impregnation into the anode matrix might be a better way to operate directly with H_2–CO syngas with a novel Ni–YSZ anode in our future work.

4. Conclusions

When fueled with H_2–CO syngas, an anode-supported SOFC with a Ni–YSZ anode has been found to be liable to carbon deposition on the edge area of the anode, which caused mechanical damage and sealing failure. A Cu–CeO_2 catalyst layer on the Ni–YSZ anode surface greatly improved the anode performance and the stability in syngas by facilitating the water gas shift reaction. An optimized single cell could be run in syngas with a composition of 48.5%H_2–48.5%CO–3%H_2O for 460 h with a stable power density output of around 280 mW cm^{-2}. Considering the thickness of the catalyst layer, CO can still make its way to the Ni–YSZ anode. A few carbon fibers were observed in the anode functional layer, which caused damage to the anode and consequent performance degradation. Therefore, carbon formation is still a critical problem over longer operation times. Besides the catalyst layer, steam reforming by catalysts impregnated into the Ni–YSZ anode matrix may prove to be a concern in our future work.

Acknowledgements

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