



Short communication

## Assessment of the performance of Ni-yttria-stabilized zirconia anodes in anode-supported Solid Oxide Fuel Cells operating on H<sub>2</sub>–CO syngas fuels

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## ABSTRACT

Anode-supported Solid Oxide Fuel Cells (SOFCs) with Ni-yttria-stabilized zirconia (YSZ) anode have been fabricated and studied using H<sub>2</sub>–CO syngas fuels. Syngas fuels with different compositions of H<sub>2</sub>–CO are supplied and the cell performance is measured at 750 °C. A high CO content has caused carbon deposition and crack formation in the Ni-YSZ anode after long-term operation, even though it is diluted with H<sub>2</sub>O and N<sub>2</sub>. However, it was found that a Cu–CeO<sub>2</sub> coating on Ni-YSZ can greatly improve the anode stability in syngas by facilitating the water gas shift reaction. The optimized single cell has run in syngas with a composition of 65%H<sub>2</sub>–32%CO–3%H<sub>2</sub>O for 1050 h without obvious degradation of its performance.

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### 1. Introduction

Solid Oxide Fuel Cells, electrochemical devices that can directly convert the chemical energy of fuels into electrical energy, have attracted great interest in recent years due to their fuel flexibility. Besides hydrogen, natural gas [1], biogas [2], ethanol [3,4], coal-derived syngas [5] even wood-derived [6] gases have been studied as fuels for SOFCs so far. Compared to other fuel cells, SOFC can better tolerate carbon monoxide and other impurities in their fuels [7].

Direct utilization of coal-derived syngas as the fuel for SOFCs not only increases the energy efficiency and reduces the operational cost of power generation, but also enables the co-production of other marketable commodities such as hydrogen, and provides flexibility for carbon dioxide sequestration [8]. Coal is often gasified for use as a fuel for SOFCs, whereby the fuel supply essentially consists of a mixture of H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>. Depending on the type of coal, however, the composition of the syngas varies widely, and this affects the SOFC performance [9].

Carbon formation is a problem that can limit the cell performance and stability when SOFCs with novel Ni-YSZ anodes are fueled with syngas. This is due to the Boudouard reaction (reaction (1)), whereby CO is converted into carbon on the anode surface. Meanwhile, CO can also serve to generate H<sub>2</sub> under SOFC operating

conditions through the water gas shift reaction (WGS, reaction (2)).



In the present study, we have fabricated anode-supported SOFCs with Ni-YSZ anodes and have measured the cell performance in H<sub>2</sub>–CO syngas fuels of different compositions. The dilution effects of nitrogen and water in the syngas have also been studied. The Ni-YSZ anode stability and carbon deposition were monitored upon discharging in syngas with high CO content. Cu–CeO<sub>2</sub>, an effective WGS catalyst, was impregnated into the Ni-YSZ anode to suppress carbon formation and to improve its long-term stability in syngas. The optimized single cell had run in syngas with a composition of 65%H<sub>2</sub>–32%CO–3%H<sub>2</sub>O for 1050 h without obvious degradation of its performance.

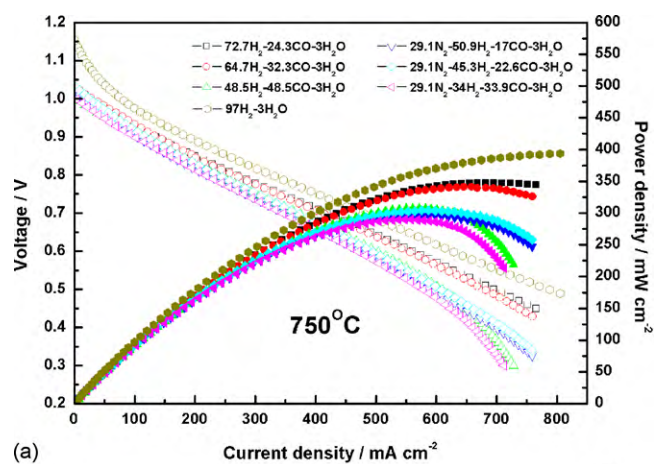
### 2. Experimental

#### 2.1. Fabrication of the single cells

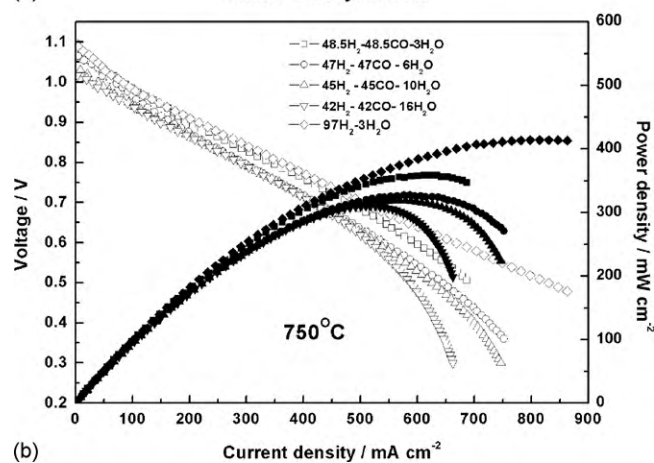
Anode-supported Solid Oxide Fuel Cells (SOFCs) were fabricated by tape casting and screen printing technology. An anode-supported electrolyte membrane composed of NiO-YSZ supported anode layer, NiO-YSZ anode functional layer, and YSZ electrolyte was fabricated by multi-layer tape casting and co-sintering, as has been typically employed by our group. Details of the process of its manufacture can be found elsewhere [10]. LSM ((La<sub>0.8</sub>Sr<sub>0.2</sub>)MnO<sub>3</sub>) slurry was screen printed onto the electrolyte surface and sintered at 1200 °C for 3 h to fabricate the cathode.

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(a)



(b)

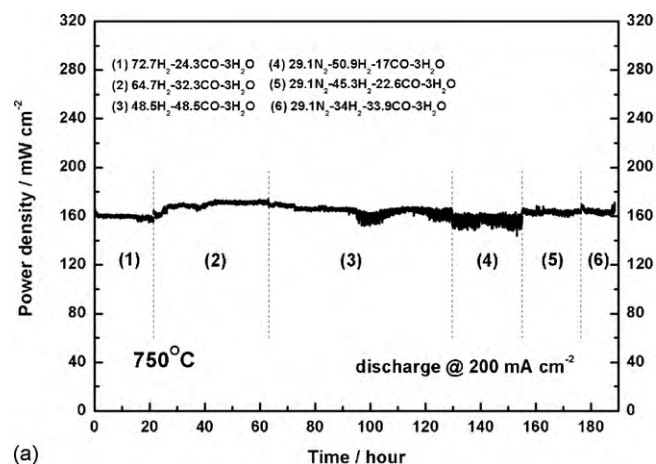
Fig. 1. Voltage (empty symbols) and power density (filled symbols) vs. current density for cell 1 (a) and cell 2 (b) in syngas fuels with different compositions at 750 °C.

Three single cells were fabricated by the aforementioned process, which were denoted as cell 1, cell 2, and cell 3. The Ni-YSZ anode of cell 3 was impregnated with aqueous solutions of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and then subjected to low temperature calcination at 450 °C to form the oxides. The Cu–CeO<sub>2</sub> impregnation load was 4 wt% of the anode weight, and the weight ratio of Cu to CeO<sub>2</sub> was 1:9.

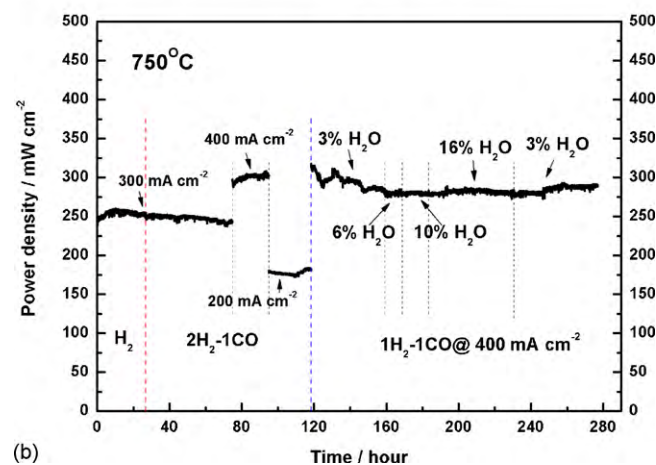
## 2.2. Characterization of single cell performance

SOFC tests were carried out in 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 surface of the anode and cathode using Au 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 H<sub>2</sub> atmosphere for several hours prior to cell testing, and the electrochemical tests were carried out at 750 °C. All the single cell anodes were evaluated according to the same testing procedure.

Mixtures of H<sub>2</sub>, CO and N<sub>2</sub>, with their compositions regulated by a set of mass-flow controllers, were used as fuels, and oxygen was used as an oxidant. The fuel and oxidant flow rates were both controlled at 40 mL min<sup>-1</sup>. A hydrator placed on a temperature controlled bath was used to humidify the inlet fuel stream. The current–voltage curves and electrochemical impedance spectra (EIS) were obtained using an Electrochemical Workstation (IM6e, ZAHNER). Impedance spectra of the electrochemical cells were



(a)



(b)

Fig. 2. Power density as a function of time for cell 1 (a) and cell 2 (b) while discharging under constant current density in hydrogen and syngas at 750 °C.

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. Ni-YSZ anode performance 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), respectively, in hydrogen and syngas. For cell 1, we studied the effect of the increased CO content in the syngas on the anode performance, while the effect of introducing steam was studied for cell 2. The OCV of cell 1 and cell 2 exceeded 1.1 V, and their maximum power densities were measured as about 400 mW cm<sup>-2</sup> in hydrogen fuel. When H<sub>2</sub> was diluted with CO, N<sub>2</sub> or H<sub>2</sub>O, similar general trends were observed, with both the OCV and the maximum power density of the single cell decreasing with increasing dilution. Considering that the cathode conditions were the same throughout, the difference in cell performance can be attributed to different anode polarizations. The decrease in performance with H<sub>2</sub>–CO–H<sub>2</sub>O syngas as fuels was because of slow diffusion and slow electrochemical reaction rates for CO and H<sub>2</sub>O [11], as was evident from the obvious limiting current density in the curve at higher CO or H<sub>2</sub>O concentrations.

Fig. 2 shows curves of power density for cell 1 (a) and cell 2 (b) as a function of time obtained by discharging at constant current

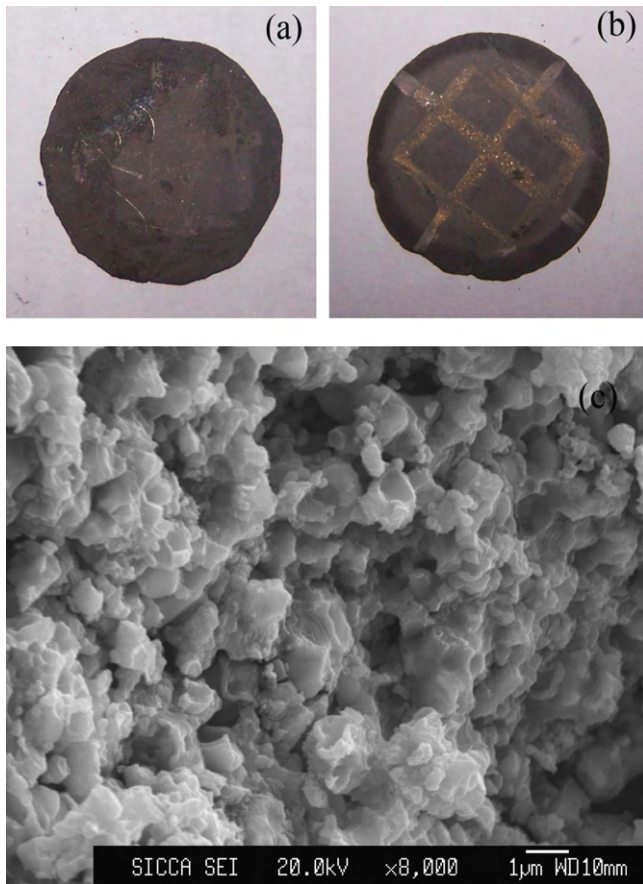


Fig. 3. Photographs of cell 1 (a) and cell 2 (b) and cross-sectional SEM image of cell 3 (c) after operation in syngas for longer than 200 h at 750 °C.

density in different syngas compositions at 750 °C. When the current density was low, typically  $\leq 400 \text{ mA cm}^{-2}$ , the cell performance showed almost no difference in different syngas compositions. This is consistent with what was showed in previous  $I$ - $V$  curves. Although the two cells displayed stable output in syngas as long as  $\sim 280$  h, there are some oscillations in the curves, which are probably due to the appearance of some micro cracks of the anode as a result of carbon deposition.

We found that carbon deposition caused by the Boudouard reaction of CO can lead to disintegration of the anode after operation, especially in its edge area where there is little current density. The photograph in Fig. 3(a) illustrates the phenomenon of anode cracking, which may lead to some leakage of fuel gas and decreases in the OCV and anode performance. The photograph in Fig. 3(b) demonstrates the intact anode surface of cell 2, although there is still some fragmentation around the edge. This may be an evidence of the effect of introducing  $\text{H}_2\text{O}$  into the syngas.

### 3.2. Cu-CeO<sub>2</sub> coated Ni-YSZ anode performance in syngas

Cu-CeO<sub>2</sub> is an effective WGS reaction catalyst, which is applied in hydrogen production by the process of steam reforming [12]. We have also used it as a catalyst layer on the surface of Ni-YSZ to run an SOFC directly on ethanol [13]. Here, the catalyst was impregnated into the anode to suppress carbon formation and to improve the anode stability. Fig. 4 shows the variation in electrochemical performance as a function of operation time of cell 3 with an impregnated anode while running in hydrogen and syngas. From Fig. 4(a), it can be seen that the cell performance in 97% $\text{H}_2$ -3% $\text{H}_2\text{O}$  is very close to

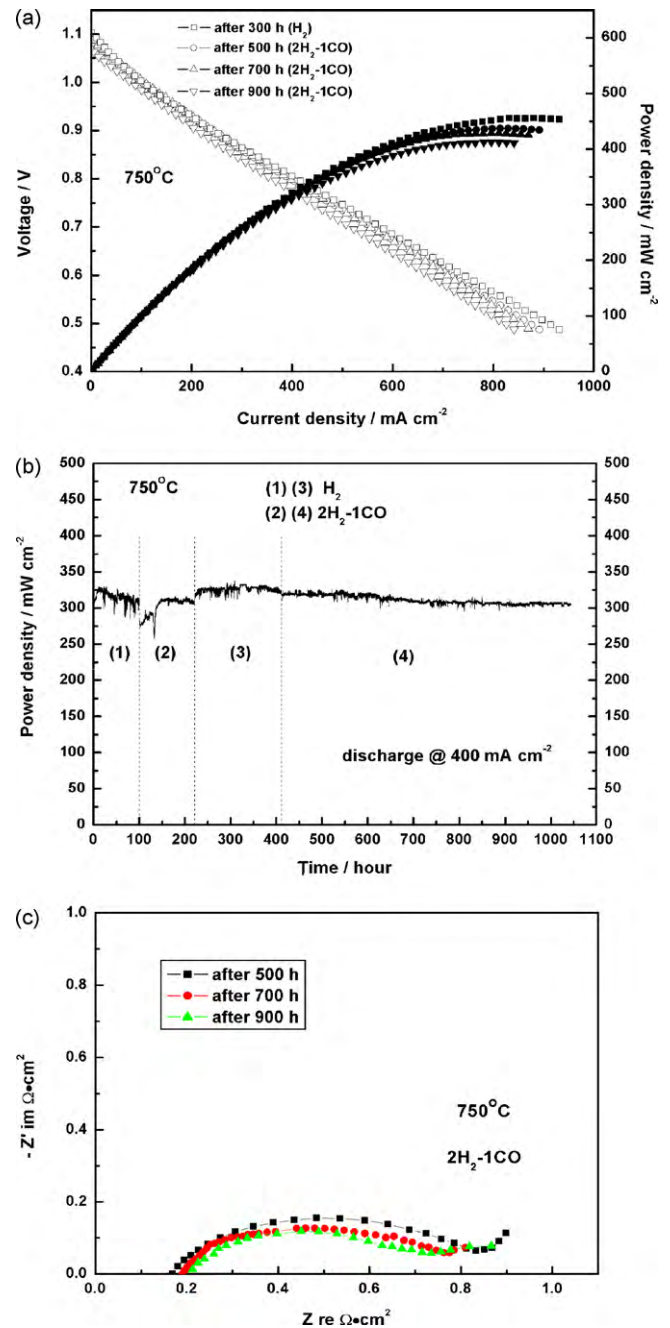


Fig. 4. Electrochemical performance and impedance spectra under open-circuit conditions as a function of operation time for cell 3 in syngas at 750 °C.

that in 64.7% $\text{H}_2$ -32.3% $\text{CO}$ -3% $\text{H}_2\text{O}$ . Moreover, even after running in syngas for 700 h, the  $I$ - $V$  curve is almost the same as that at the beginning. The Cu-CeO<sub>2</sub> catalyst is effective in promoting the reaction of CO with  $\text{H}_2\text{O}$  produced by the electrochemical oxidation of hydrogen to form additional  $\text{H}_2$ . Meanwhile, the removal of CO suppresses carbon deposition in the anode. The cross-sectional SEM image in Fig. 3(c) demonstrates that little carbon fiber was formed in the anode matrix except for some small impregnated Cu-CeO<sub>2</sub> particles. The curve in Fig. 4(b) shows that the output of the cell in hydrogen and syngas remained stable for as long as 1050 h. The degradation in the last 600 h operation time in syngas is less than 5%. Corresponding to these results, the impedance spectra in Fig. 4(c) indicates that the ohmic resistance of the cell increased a little, from  $0.168 \Omega \text{ cm}^2$  to  $0.212 \Omega \text{ cm}^2$ , and this is

probably the reason for the degradation. However, the polarization resistance of the cell decreased with time due to electrode activation. It is for this reason that the cell performance could remain stable. The Cu–CeO<sub>2</sub> load in the anode and the conversion efficiency of the CO feed are important for improving the stability of the anode, which can be subsequently optimized by analyzing the exit gas.

#### 4. Conclusions

The stability of the Ni-YSZ anode in syngas was limited by carbon formation through the Boudouard reaction. The deposited carbon can cause anode damage, followed by seal failure and performance degradation. However, this may be overcome by introducing H<sub>2</sub>O into the syngas fuel, albeit at the expense of some loss in the electric power output. Cu–CeO<sub>2</sub> coating on Ni-YSZ can greatly improve the anode performance and stability in syngas by facilitating the water gas shift reaction. An optimized single cell had run in syngas with a composition of 65%H<sub>2</sub>–32%CO–3%H<sub>2</sub>O for 1050 h with a stable power density output of around 300 mW cm<sup>-2</sup>. However, the Cu–CeO<sub>2</sub> impregnation load and the conversion of CO feed need to be optimized in future work to improve the anode stability over longer operation times.

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