

Use of a catalyst layer for anode-supported SOFCs running on ethanol fuel

Xiao-Feng Ye, S.R. Wang^{*}, Z.R. Wang, L. Xiong, X.F. Sun, T.L. Wen

Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS), 1295 Dingxi Road, Shanghai 200050, PR China

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Abstract

Solid oxide fuel cells (SOFCs) operating directly on hydrocarbon fuels have attracted much attention in recent years. A two-layer structure anode running on ethanol was fabricated by tape casting and screen printing technology in this paper, the addition of a Cu–CeO₂ catalyst layer to the supported anode surface yielded much better performance in ethanol fuel. The effect that the synthesis conditions of the catalyst layer have on the performances of the composite anodes was investigated. Single cells with this anode were also fabricated, of which the maximum power density reached 566 mW cm⁻² at 800 °C operating on ethanol steam. Long-term performance of the anodes was presented by discharging as long as 80 h without carbon deposition.

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1. Introduction

A major advantage of solid oxide fuel cells (SOFC) is that they have much greater fuel flexibility, which allows SOFC to operate, in principle, on any combustible fuel [1]. SOFCs operating directly on hydrocarbon fuels without external reforming, are expected to be an important technology for energy generation in the near future. Regarding the current oil crisis and the shortage of fossil fuels, ethanol is considered to be an attractive green fuel for SOFCs due to several advantages such as easiness and safety in storage, handling and delivering with existing supply infrastructure [2]. It is also renewable from various biomass sources, and easily soluble with necessary amount of water for internal reforming.

Ni/YSZ (yttria stabilized zirconia) cermet is now the most commonly used anodes in SOFCs due to their high electrochemical activity for H₂ oxidation and demonstrated long-term stability at SOFC operating conditions [3,4]. However, Ni/YSZ suffers a number of drawbacks while using hydrocarbon fuels, notably the carbon deposition, which covers the active sites of

the anodes, resulting in the rapid degradation of the cell performance. High steam/carbon ratio is necessary to suppress the carbon deposition, which lowers the electrical efficiency of the system.

In order to overcome the disadvantages of Ni/YSZ cermet anode, several alternative materials were investigated as potential anodes in recent years. Gorte and his co-workers avoided the problem of carbon deposition by using Cu–CeO₂ anode [1,5–8], in which copper acted as current collector while ceria provided a high catalytic activity for hydrocarbon reforming. Due to the low melting point of copper and its oxides, an alternative method in place of traditional high temperature sintering was developed on basis of tape casting and wet impregnation. We have been focusing on fabricating Cu–CeO₂–ScSZ (scandia stabilized zirconia) anode by similar method and have gotten good and stable performance in hydrogen and ethanol with this anode [9]. However, the fabrication process needs time after time wet impregnation and low temperature calcinations, which increases the cost. Zhan and Barnett focused on adding a Ru–CeO₂ surface catalyst layer to allow the propane partial oxidation reaction [10]. However, its use is limited by the high price of Ru and evaporation above 1200 °C to produce volatile RuO₄ species [4].

In this paper, we fabricated a two-layer structure anode running on ethanol by tape casting and screen-printing technology, which are both cost-effective and feasible. The addition of a

^{*} Corresponding author. Tel.: +86 21 52411520; fax: +86 21 52413903.

E-mail addresses: yexf@mail.sic.ac.cn (X.-F. Ye), srwang@mail.sic.ac.cn (S.R. Wang).

Cu–CeO₂ catalyst layer to the supported anode surface yielded much better performance in ethanol fuel by internal reforming. The effect that the synthesis conditions of the catalyst layer have on the performances of the composite anodes was investigated. Single cell with this anode was also fabricated, of which the maximum power density reached 566 mW cm⁻² at 800 °C operating on ethanol steam. The long-term performance of the anodes was presented by discharging as long as 80 h, from which the possible reason for cell performance degradation was also discussed.

2. Experimental

2.1. Catalyst preparation

In order to obtain homogeneous catalyst, the Cu–CeO₂ composite oxide was prepared by the citric method as follows. An aqueous solution containing all required ions as metal nitrates (Cu(NO₃)₂·3H₂O, (NH₄)₂Ce(NO₃)₆·6H₂O) was first stirred at room temperature, to which an equivalent of citric acid (C₆H₈O₇·H₂O) of per total metals was then added. The solution was stirred for 30 min and held at boiling temperature for 60 min to evaporate water, resulting in fine ash of pale green colour. The resultant ash was then fired at 800 °C for 3 h to form the catalyst powder. Three kinds of catalysts with different Cu/CeO₂ weight ratio of 1:1, 1:2 and 1:3 were fabricated by this way. The Cu/80%CeO₂–20%ZrO₂ and Cu/60%CeO₂–40%Al₂O₃ (metal and oxide support with weight ratio of 1:2) catalysts were also prepared by the similar citric method using Zr(NO₃)₄·5H₂O and Al(NO₃)₃·9H₂O.

2.2. Fabrication of unit-cells

A typical single cell used in the present work consisted of the following four distinct layers, which are shown in Fig. 1 (a) porous Cu–CeO₂ catalyst layer, (b) porous Ni/YSZ-supported anode, (c) dense ScSZ electrolyte and (d) porous PCM cathode.

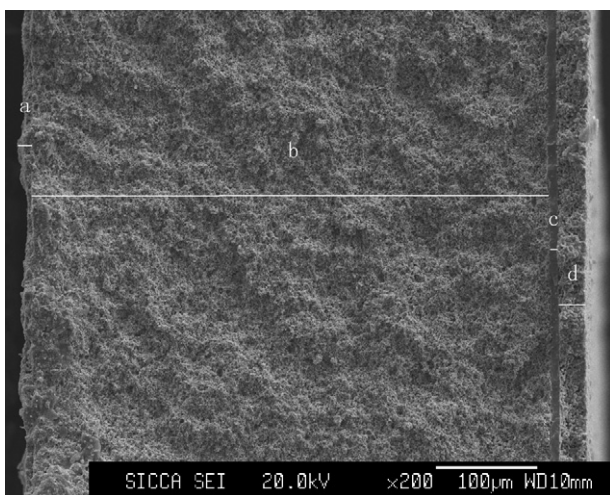


Fig. 1. A SEM micrograph of a fractured cell showing four layers, (a) porous Cu–CeO₂ catalyst layer, (b) porous Ni/YSZ-supported anode, (c) dense ScSZ electrolyte and (d) porous PCM cathode.

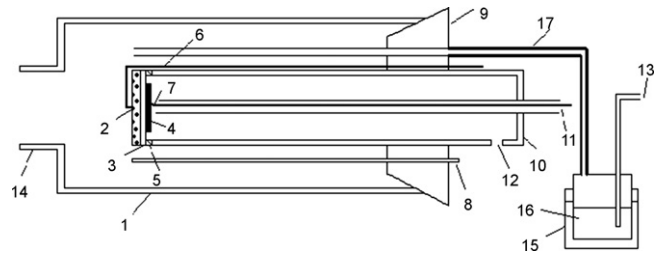


Fig. 2. Schematic drawing of cell testing set up, (1) furnace tube, (2) anode, (3) electrolyte, (4) cathode, (5) glass seal, (6) anode lead wire, (7) cathode lead wire, (8) thermocouple, (9) seal plug, (10) alumina tube, (11) oxygen inlet, (12) oxygen outlet, (13) fuel inlet, (14) fuel outlet, (15) water bath, (16) ethanol and water, (17) heating tape and copper tube.

PCM ((Pr_{0.7}Ca_{0.3})_{0.9}MnO₃) cathode. The thickness of each layer is about 30 µm, 600 µm, 15 µm and 40 µm, respectively. Cell fabrication procedure is briefly described in what follows. The anode-supported electrolyte dual layer membrane was produced by multilayer tape casting and co-sintering. A mixture of 50 wt% nickel oxide (Inco Ltd., Canada), 30 wt% 3YSZ and 20 wt% 8YSZ (Tosoh Co.) powders were used to make an anode substrate, while ScSZ (99.99% pure, Daiichi Kigenso, Japan) powders used as electrolyte. The electrolyte slurry comprised of electrolyte powders and organic ingredients such as binder (poly-vinyl-butyl), dispersant (triethanolamine), plasti-

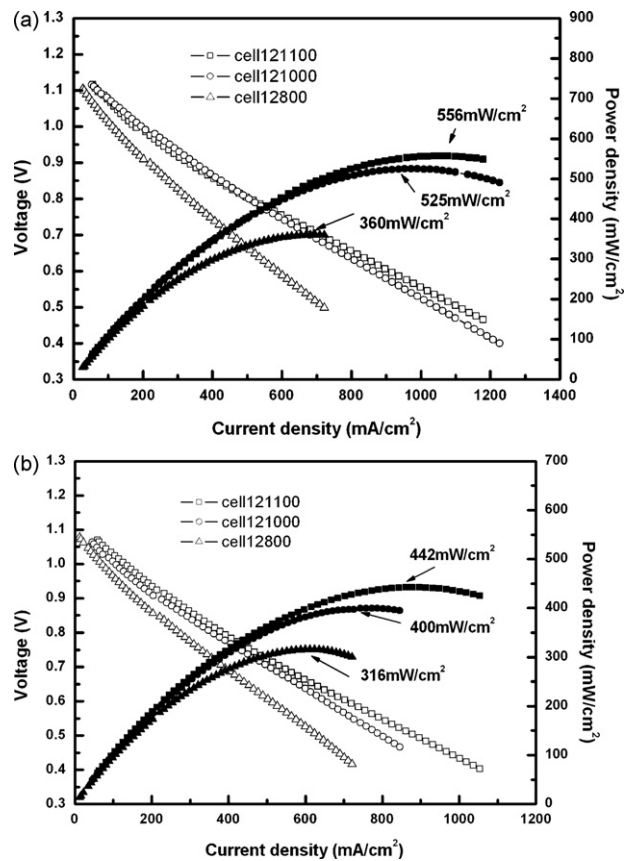


Fig. 3. Voltage (open) and power density (closed) vs. current density for cells with different catalyst layer heat-treatment temperature in hydrogen (a) and ethanol steam (b) at 800 °C.

cizer (mixture of polyethylene glycol and dibutyl-*o*-phthalate) and solvents (azeotropic mixture of butanone and ethyl alcohol) was ball-milled, tape-cast and allowed to dry at room temperature for 24 h. The anode slurry containing pore formers (ammonium oxalate, 10 wt% of anode powders) was then fabricated and cast on the top of the electrolyte green tape and allowed to dry for 24 h. The composite structure was sintered at 1400 °C for 3 h. The cathode of 1.4 cm² area was fabricated by screen-printing a slurry containing PCM ((Pr_{0.7}Ca_{0.3})_{0.9}MnO₃, provided by co-workers in our lab) onto the surface of the dense ScSZ electrolyte and sintering at 1200 °C for 3 h. Finally, the slurry of Cu–CeO₂ catalyst was screen-printed onto the supported anode surface, which is of 4.9 cm² area. Then they are sintered at 800 °C, 1000 °C or 1100 °C. These single cells are denoted as cell12800, cell121000, cell121100, cell111100 and cell131100, respectively, of which the first two numbers are the weight ratio of copper versus ceria in the catalyst, and the last four numbers are the heat-treatment temperature of the screen printed catalyst layer.

2.3. Characterization of single cell performance

The microstructure and morphology of the cell structure were examined by scanning electron microscopy (SEM, JXA-8100, JEOL Co. Ltd., Japan). SOFC tests were carried out in a single cell test set up which was illustrated in Fig. 2. A Pt mesh and Au lead wire as the current collector were attached to the surface of the anode and cathode using a Pt paste, and a four-probe configuration was adopted in the electrochemistry test. The cathode side of the structure was then attached to an alumina tube using Pt paste and the edges were sealed using a glass ring. All the anodes were evaluated with the same testing procedure. The anodes were fully reduced in H₂ atmosphere at 800 °C for several hours prior to cell testing. In order to avoid copper sintering and keep the anode performance, the measurement was carried out at the temperature of 750 °C and 800 °C.

Hydrogen or gasified ethanol–water mixture (with volume ratio 2:1) were used as fuel and oxygen was used as oxidant. The fuel and oxidant flow rate were all controlled at 25 mL min⁻¹, and the liquid fuel was vaporized by water bath (70 °C) and then

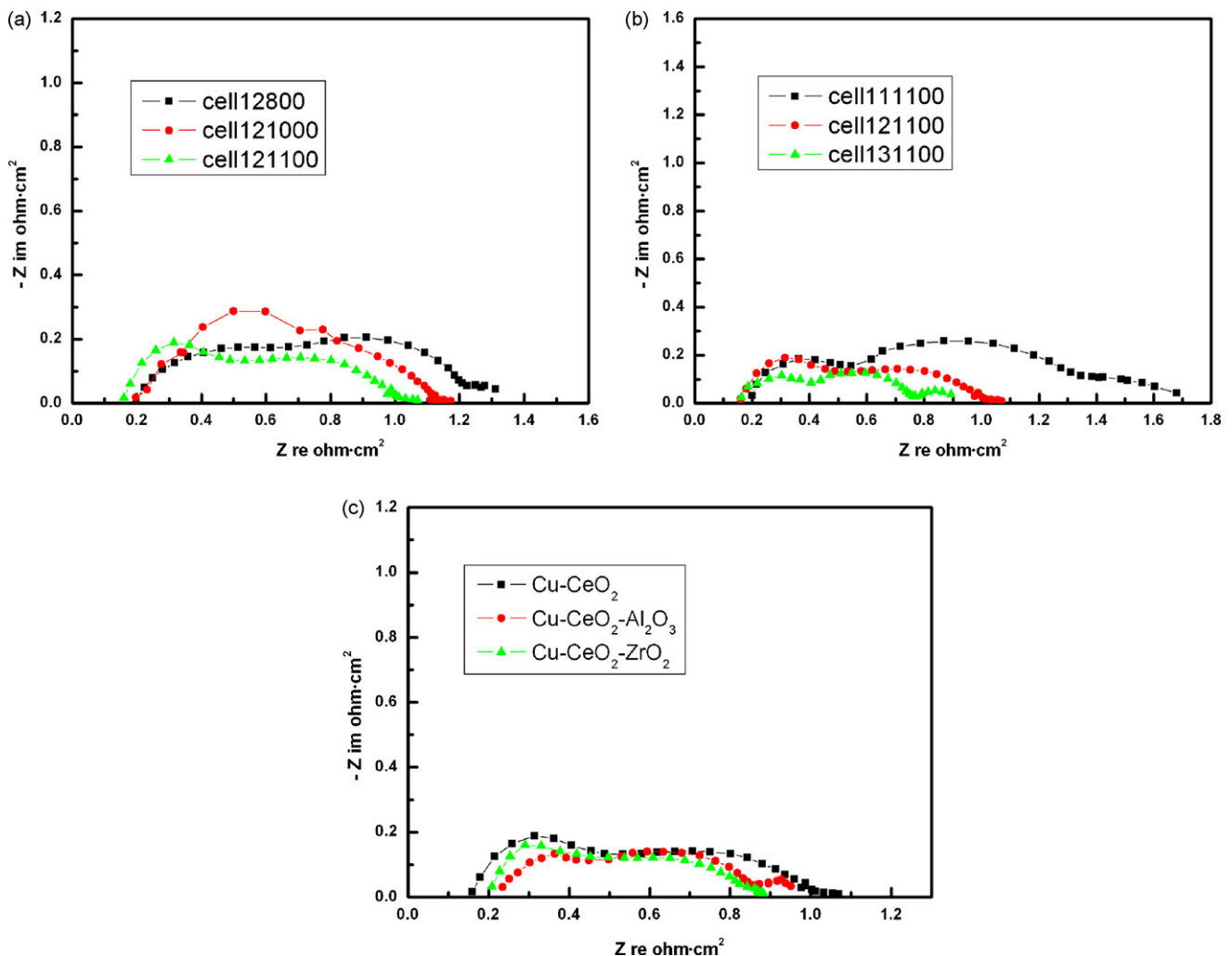


Fig. 4. Impedance spectra for cells with (a) different catalyst layer heat-treatment temperature, (b) different Cu/CeO₂ weight ratios catalyst layer and (c) different catalyst composition while running on ethanol steam at 800 °C.

brought onto the anode surface by nitrogen. The current–voltage curves and electrochemical impedance spectroscopy (EIS) was obtained using an Electrochemical Workstation (IM6e, ZAHNER). The impedance spectra of the electrochemical cell were recorded at open circuit voltage (OCV) over the frequency range of 100 kHz to 0.008 Hz with excitation potential of 20 mV.

3. Results and discussion

3.1. Heat-treatment temperature of catalyst layer

Anode-supported single cells with Ni/YSZ anode in our lab prepared by multilayer tape casting and co-sintering show good performance for hydrogen [11]. However, while adding a catalyst layer to the supported anode surface, the adhesion between the two layers greatly affects the performance of composite anode structure. In our work, we calculated the catalyst layer (Cu/CeO₂ weight ratio all of 1:2) at 800 °C (the maximum operation temperature), 1000 °C and 1100 °C (a little lower than the melting point of CuO) on different single cells, which were tested in hydrogen and ethanol steam and discharged for a long time to study the effect of heat-treatment temperature of catalyst layers having on the anode microstructure and performance.

Fig. 3 is the curves of voltage and power density versus current density for the three cells while running on humidified hydrogen (a) and ethanol stream (b) at 800 °C, from which we can see that with the increase of heat-treatment temperature, the single cells showed better performance, and for cell121100, the maximum power density in hydrogen and ethanol steam reached 556 mW cm⁻² and 442 mW cm⁻², and while discharging at 0.6 V, the utilization factor for H₂ and EtOH is about 33% and 43%, respectively. Results of impedance spectra obtained at open circuit voltage for the three cells in ethanol steam presented in Fig. 4(a) confirmed that the anode with high heat-treatment temperature showed smaller polarization resistance, which revealed that a higher temperature heat-treatment gives good adhesion between the two layers in anode. The SEM images in Fig. 5(a) of interface in cell121100 shows that the catalyst layer is well adhered to the supported anode even after 80 h operation in ethanol, from which we can also see the two layers are relatively porous for gas diffusion.

3.2. Cu/CeO₂ weight ratios

In previous work, we found that in Cu–CeO₂–ScSZ anode, copper plays much important role because it provides the conductivity and connectivity path of the anode system [9]. So when the ceria amount in the anode reaches some value, the increase of copper amount will improve the anode performance by providing better conductive network. In the dual layer anode structure, however, the case is probably that ethanol steam reforming takes place in the catalyst layer first, and then the supported anode catalyses the oxidation of the products of internal reforming and provides the conductivity of the whole anode, which means that the catalysis of ethanol on ceria is much more important in the surface layer.

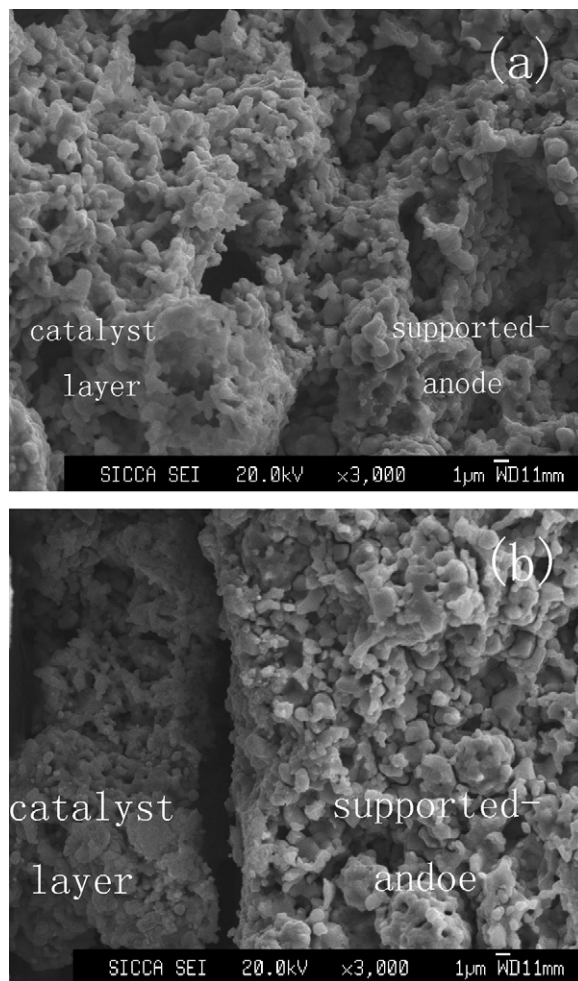
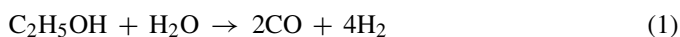


Fig. 5. SEM images of the interface between the catalyst layer and the supported anode of cell121100 (a) and cell131100 (b) after 80 h operation in ethanol steam.

To determine the different role of copper and ceria in the catalyst layer, catalysts with three Cu/CeO₂ weight ratios of 1:1, 1:2 and 1:3 (catalyst layer all calcinated at 1100 °C) were prepared and compared by single cell performances. Fig. 6 demonstrates the voltage and power density versus current density curves for these cells measured at 800 °C, and cell131100 shows the best performance with power density of 598 mW cm⁻² and 566 mW cm⁻² in hydrogen and ethanol steam, respectively.

An interesting fact is that the power density of cell131100 in ethanol steam is very close to that in hydrogen. As we know, the two reactions (1) and (2) mainly occurs when ethanol steam are fed to the catalyst, since Ni is much active a catalyst for hydrogen oxidation than carbon monoxide oxidation, performance in hydrogen is better than in ethanol. Probably when ceria in the catalyst increased, the catalyst is much effective for hydrogen production with high selectivity for reaction (2), and the water gas shift of (3) is also a possible reaction to generate hydrogen. The impedance spectra in Fig. 4(b) also demonstrated that cell131100 had much smaller polarization resistance than cell121100 and cell111100 possibly because of much more hydrogen production and its quicker diffusion.



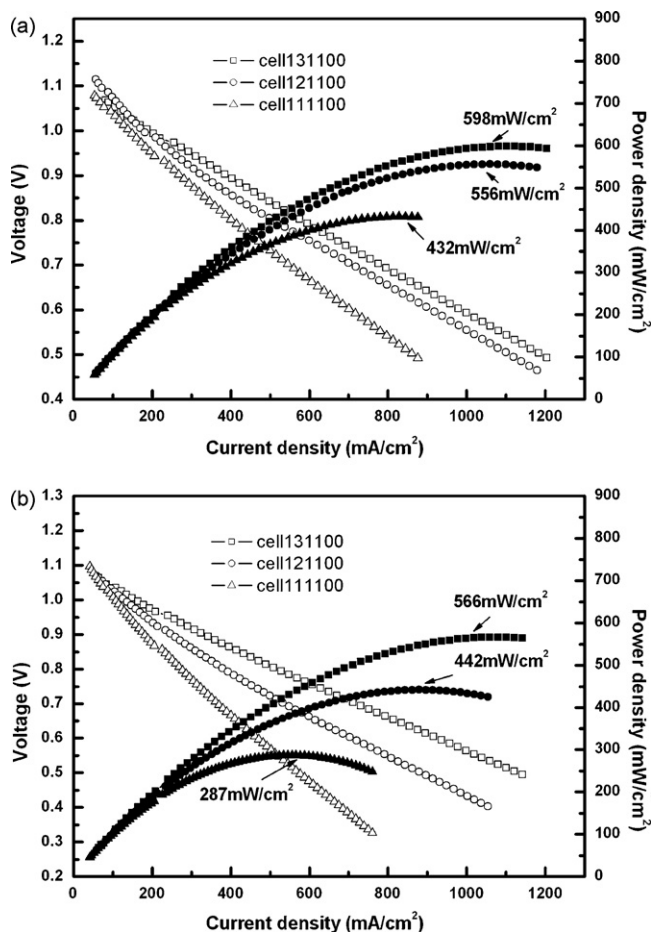
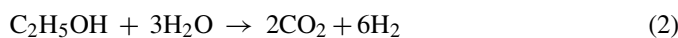


Fig. 6. Voltage (open) and power density (closed) vs. current density for cells with different Cu/CeO₂ weight ratios in hydrogen (a) and ethanol steam (b) at 800 °C.



3.3. Catalyst composition

It is well known that metal-supported ceria is an effective catalyst for ethanol steam reforming (ESR), which has been thoroughly studied in recent years [12–16]. Duprez et al. [13] proposed a bi-functional mechanism where the hydrocarbon to be reformed would be activated on the metal particle and the water would be activated on the support as hydroxyl groups. In such a scheme, oxide supports with high OH groups surface mobility should be considered as promoters in the ESR, and Aupretre et al. [15] also found that the activity of the catalyst in the ESR increases as the OH group mobility at the catalyst surface increases with the addition of oxide such as ZrO₂ and Al₂O₃.

Cu/CeO₂–ZrO₂ and Cu/CeO₂–Al₂O₃ catalysts were also prepared and applied to the supported anode surface to improve the anode performance due to their better catalysis activity, which was proved by the single cell performance of the three cells in Fig. 7. The maximum power density of Cu/CeO₂–ZrO₂ and Cu/CeO₂–Al₂O₃ single cell decreased to 520 mW cm^{–2} and

529 mW cm^{–2} in hydrogen, compared to 556 mW cm^{–2} of the Cu/CeO₂ single cell, due to their lower electronic conductivity, which exhibited as a little bigger ohmic resistance in impedance spectra of Fig. 4(c). However, with much higher yield of hydrogen production in ethanol steam reforming, their performance in ethanol steam increased from 442 mW cm^{–2} to 519 mW cm^{–2} and 493 mW cm^{–2}.

3.4. Long-term performance

Carbon deposition on steam reforming catalysts is a problem known to petrochemical industry for a long time, especially on presence of nickel [17]. We used copper in the catalyst layer, which is inert for carbon formation, however, considering nickel in the supported anode, the long-term stability of the two-layer structure anode should be studied to make sure whether coking occurs while using ethanol steam for a long time.

Fig. 8 is the curves of the power density for different cells as a function of time by discharging at 0.6 V in ethanol steam. In all these cells, cell 121100 shows the best stability with power density range around 350 mW cm^{–2} without any degradation. Cell121000 and Cu/CeO₂–ZrO₂ cell showed a little decrease at the end of the test time, however, the power density of cell131100 gradually dropped from 500 mW cm^{–2} to 300 mW cm^{–2}, and

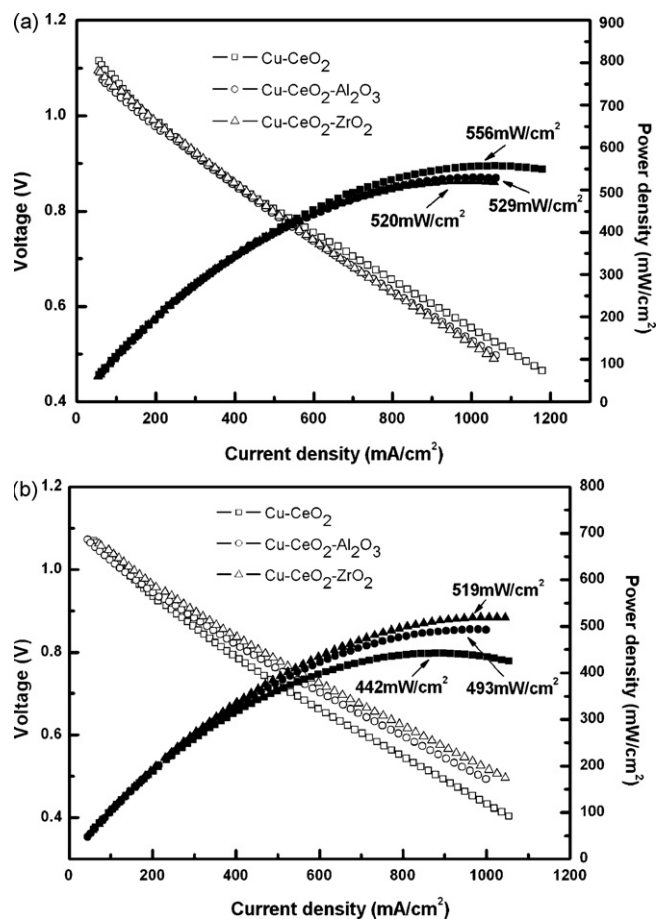


Fig. 7. Voltage (open) and power density (closed) vs. current density for cells with different catalyst composition in hydrogen (a) and ethanol steam (b) at 800 °C.

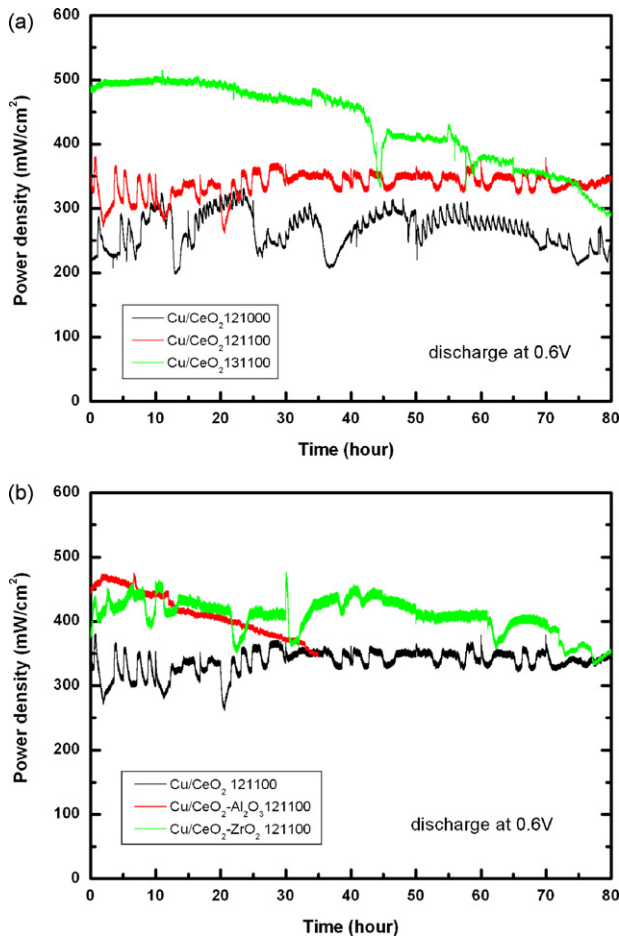


Fig. 8. Power density at 0.6 V as a function of time for different cells running on ethanol steam at 800 °C.

Cu/CeO₂–Al₂O₃ cell quickly degenerated from 470 mW cm⁻² to 350 mW cm⁻² in the first 35 h.

In an attempt to gain more information about the long-term stability of the anode, in Fig. 9 we also recorded the impedance spectra of cell121100 (a) and cell131100 (b) at open circuit voltage after every 20 h. During the operation time, the ohmic resistance of cell121100, which is the real-axis intercept at high frequency, increased a little from 0.15 Ω cm² to 0.19 Ω cm², while the polarization resistance decreased a little due to electrode activation. For cell131100, the tendency in the first 40 h was very similar to cell121100, however, in the last 40 h, the ohmic resistance increased to about 0.3 Ω cm², and the polarization resistance was two times as the beginning, which probably is the reason for cell degradation in Fig. 7(a). The migration of copper at high operation temperature is a possible reason for this ohmic resistance increase. On the other side, an obvious delamination, which is probably resulted from the different thermal expansion coefficient between ceria and zirconia, is seen in the SEM image of Fig. 5(b), and for cell with Cu/CeO₂–ZrO₂ and Cu/CeO₂–Al₂O₃ catalyst layer, the same phenomenon was observed. Apparently, this is why the ohmic and polarization resistance of these cells increases and the cell performance degraded. While increasing CeO₂ content or adding zirconia and alumina, a higher heat-treatment temperature after screen-

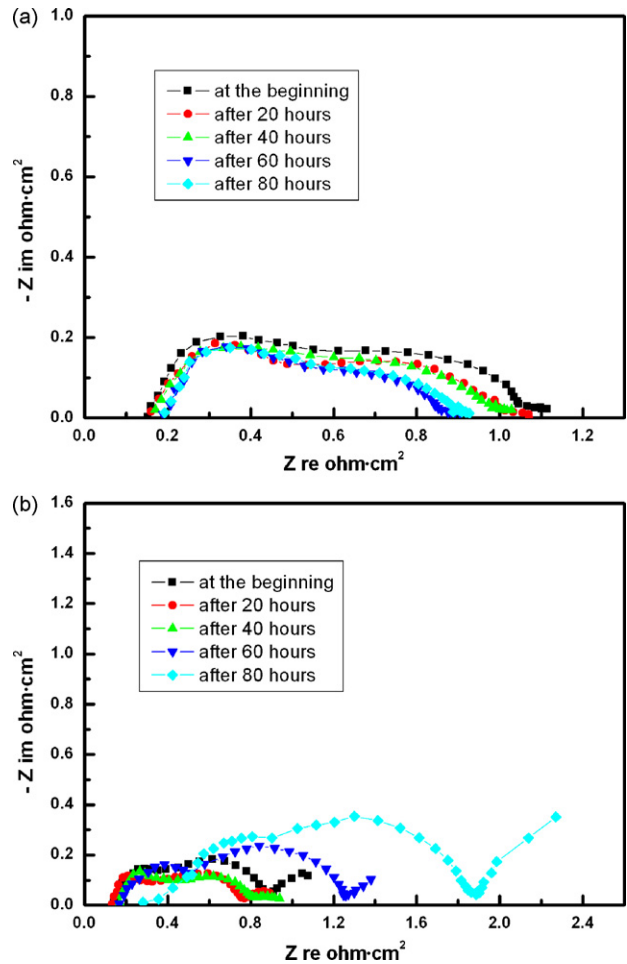


Fig. 9. Impedance spectra for cell121100 (a) and cell131100 (b) as a function of operation time running on ethanol steam at 800 °C.

printing is probably necessary for the catalyst layer to combine well with the supported anode.

Some of the ethanol will make its way to the Ni–YSZ matrix during operation considering the thickness of the Cu–CeO₂ catalyst layer. After our 80 h operation in ethanol, there is little carbon formation seen in the Ni–YSZ matrix from the SEM images in Fig. 5. However, whether there is any carbon deposition after even longer time operation still needs to be concerned in our next stage work.

4. Conclusions

A two-layer structure anode running on ethanol was fabricated by tape casting and screen printing technology in this paper, and the addition of a Cu–CeO₂ catalyst layer to the support anode surface yielded much better performance in ethanol fuel probably due to the ethanol steam reforming reaction takes place in the catalyst layer. Different from the Cu–CeO₂–ScSZ anode system we have fabricated before, in the catalyst layer ceria plays much important role. Good combination between the catalyst layer and the support anode is necessary to reduce contact resistance between layers and improve the stability of the anode system. The single cell with Cu–CeO₂ (with weight

ratio 1:2) catalyst layer calcinated at 1100 °C shows both good performance and long-term stability in ethanol steam with power density keep around 350 mW cm⁻² for 80 h without carbon formation, and the addition of Al₂O₃ and ZrO₂ has improved the activity of the Cu–CeO₂ catalyst for ethanol steam reforming. Cracking and delamination of the catalyst layer is the main reason for performance degradation of cells with this two-layer structure anode. Fabrication of this structure for long-term stability continues to be a potential concern, and the conversion over ethanol feed needs determining to improve internal reforming efficiency by analyzing the exit gas later.

Acknowledgements

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