

Combined Cu-CeO₂/YSZ and Ni/YSZ dual layer anode structures for direct methane solid oxide fuel cells

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Summary

In this study, a conventional Ni/yttria-stabilized zirconia (YSZ) anode and a new Cu-CeO₂-YSZ anode structure were assembled in an attempt to combine the advantages of both structures for use in direct methane solid oxide fuel cells. For this purpose, only a limited region ($\leq 20 \mu\text{m}$) of NiO/YSZ was deposited at the boundary of the electrolyte to benefit from the superior catalytic activity of Ni in the cells, while the rest of the cell benefited from the Cu-CeO₂-YSZ anode structure, which does not cause cracking reactions. First, the effects of different pore formers on the anode skeleton, as well as the interactions of the Ni-Cu species in the anode skeleton, are discussed. Then, the NiO/YSZ-interlayer-containing button cells with different thicknesses (≤ 20) and different ratios of NiO (40 wt%, 50 wt%, and 60 wt%) were studied. After the examination of the cells, 2 model cells with outstanding performance and 2 additional internal reference cells, conventional Ni/YSZ and Cu-CeO₂-YSZ, were scaled up, and performance analysis and long-term stability studies were carried out. As a result, for solid oxide fuel cells with increased carbonization resistance (around 6% performance loss due to carbonization after 100-hour stability testing) and 86.1% of the initial performance of the conventional Ni/YSZ anode structure, a 15- μm -thick 40 wt% NiO/60 wt% YSZ interlayer with a dual layer anode structure is proposed.

KEYWORDS

combined anode, methane, NiO/YSZ interlayer, solid oxide fuel cells

1 | INTRODUCTION

Use of hydrogen as a fuel in solid oxide fuel cells, which are considered candidate devices to meet the ever-growing need for energy, has developed significantly, and prototype devices with kilowatt capacities have been produced by several companies. Furthermore, combined heat and power generation systems have also been demonstrated. Despite this, the commercialization of solid oxide fuel cells has not yet been completed because hydrogen is not a primary energy source.¹⁻⁴

Most of the hydrogen produced by industry is produced by the steam reforming reaction of hydrocarbons (>90%). The steam reforming reaction is endothermic; thus, hydrogen production is energy intensive. Moreover, the difficulties and high costs of storing and transporting hydrogen limit the economics of systems that use hydrogen as an energy source. Therefore, it is important to develop and use a direct supply of hydrogen including fuel, in order to avoid costly hydrogen production, storage, and transportation steps.⁵⁻⁷

In solid oxide fuel cells, it is possible to use hydrocarbons directly as a fuel without reforming.⁸⁻¹⁰ For

hydrogen fuel, the most favorable anode structure is a nickel catalyst; however, the reaction conditions (ca. 800°C) cause coking of the hydrocarbons. Although Ni/yttria-stabilized zirconia (YSZ) cermet (ceramic-metal) systems show excellent initial performance, even in the direct use of hydrocarbon as a fuel,^{11–13} carbon deposits on the surface make fuel transport to the active three-phase boundaries (TPBs) difficult and reduce the mechanical strength of the cell by blocking the pores.^{14,15}

Thus, instead of using Ni, mixed oxides such as the Cu-CeO₂ system, different perovskite structures, and active catalytic materials for oxidation reactions (eg, La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ}) have been developed. Nevertheless, none of these developed structures approach the initial performance of Ni/YSZ.^{16–19}

Another approach proposed in the literature to prevent coking-induced cell degradation is the use of a layered anode structure.^{20,21} Many studies have reported that active TPB regions are not present in the whole cell structure, and there is an oxygen gradient from the electrolyte boundary to the electrode. That is, the electrolyte boundary is an oxygen-rich area, and the amount of oxygen decreases with increasing distance from the electrolyte boundary.^{22,23} Thus, after a certain depth, nickel and similar cracking catalysts in the structure are left with insufficient oxygen and fuel. Therefore, it is impossible to prevent carbonization reactions. In our earlier work,²⁴ we investigated an active Ni/YSZ interlayer for Cu-based direct-methane solid oxide fuel cells. Based on the literature and our work, we have assumed that “the carbonization can be prevented or minimized by using an anode with a suitable Ni ratio and appropriate Ni/YSZ layer thickness because the electrochemical oxidation rate in the anode will be higher than the carbon formation rate,” and this is the basis of the present work. In regions where carbonization is likely to occur in the presence of a catalyst active for cracking (oxygen ions are inadequate to prevent coking, but oxygen ions are not consumed), performance improvement by utilizing the Cu-CeO₂ structure is particularly valuable (as summarized in Figure 1).

As detailed in Figure 1, the Ni/YSZ thickness is not the last point reached by the O^{2–} ions carried from the electrolyte and diffusing through the anode. However, the rate of oxidation is higher than the rate of carbonization; therefore, carbonization will not occur in the boundary region. It is possible to transport O^{2–} ions to the area beyond the Ni/YSZ layer, even though the amount of O^{2–} is small. However, the problem of carbonization in the presence of Ni or another cracking catalyst (Fe, Co, or Pt) in the upper region persists. Therefore, to continue the oxidation reaction in the low O^{2–} concentration layer, an oxidation catalyst with

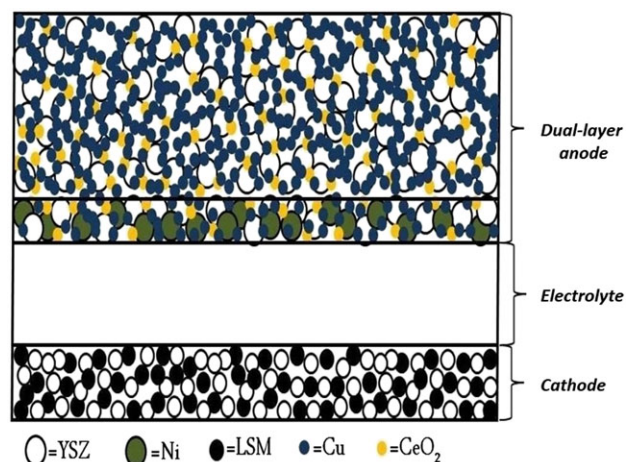


FIGURE 1 Schematic representation of the dual layer anode structure worked in the study [Colour figure can be viewed at wileyonlinelibrary.com]

a non-cracking oxide structure is required. For this purpose, the well-known Cu-CeO₂ structure can be used as the top layer.^{25–29} Here, CeO₂ is the oxidation catalyst, and Cu is an excellent electronic conductor; Cu also has the advantage of being inactive for the cracking reaction. In the structure proposed in Figure 1, there are 3 critical points.

- i. Optimum Ni/YSZ layer thickness.
- ii. Ni/YSZ ratio at critical thickness.
- iii. The Cu-CeO₂ ratio in the upper layer.

The first 2 parameters are important in terms of carbon deposition, and the significance of this has been discussed earlier. The third parameter is also very important because of the TPB definition; that is, “if the electrons generated in the reaction zone cannot be delivered to the current collector by means of an electron conduction path, then that reaction zone makes no contribution to performance.” Therefore, an electronic transmission path is needed in the cell. For this reason, the Cu/CeO₂ ratio in the upper layer is critical, and we have analyzed this previously.³⁰

In this study, the effect of different pore formers on the anode skeleton was investigated. The interactions of Ni and Cu in the anode structure were analyzed by ex situ X-ray diffraction (XRD) analysis. Cells with Ni-containing interlayers (40 wt%, 50 wt%, and 60 wt% NiO/YSZ and 5, 10, 15, and 20 μm NiO/YSZ layers) and a Cu-CeO₂ top layer (a combined anode structure) were prepared. The performance of the cells for short-term use with hydrogen and methane has been examined. After an investigation using button cells, scale-up was carried out for selected samples, and the long-term performance is discussed.

2 | MATERIALS AND METHODS

Potato starch (Merck), graphite (Fluka), activated carbon (Vulkan XC-72R), and cornstarch (Pakmaya) were used as pore formers. To examine the effect of the pore formers only, no other components were used in these investigations. The relevant pore formers were mixed mechanically in a wet environment to contain 50 wt% YSZ (FCM) and 50 wt% pore-former. After drying, the powder mixture was pelletized with a 13-mm Ø die with a hydraulic press. Sintering was then carried out at 1450°C for 6 hours. Scanning electron microscopy (SEM) examinations were made on the surface of the disks.

Then *ex situ* XRD analysis was carried out in the porous anode skeleton for the investigation of the calcination and reduction behaviors of the species. The interaction of Cu and Ni was investigated in the ceramic YSZ scaffold. For this reason, a dual-layer (dense YSZ + porous YSZ) structure was prepared by a tape-casting/laminating/co-sintering method, as described in our previous work.²⁵ Briefly, the powders were mixed with deionized (DI) water and D-3005 dispersant (Rohm & Haas). The pH was adjusted to 9 to 10 with NH₄OH and ball-milled for 24 hours to obtain a homogeneous suspension. After ball-milling, poly(vinyl alcohol) (PVA, 8% by weight in DI-water, BDH) as a binder, polyethylene glycol (PEG, Merck), and glycerol (Sigma-Aldrich) as a plasticizer were mechanically mixed with the suspension for 2 hours. Then, the slurry was cast onto a glass carrier via a doctor blade at a constant casting speed of 4 m min⁻¹. The anode and electrolyte slurry ingredients are given Table 1.

The 2 tapes were laminated together, cut as discs with a diameter of 16 mm and co-sintered at 1450°C for 6 hours. Then, Cu (NO₃)₂·3H₂O (Sigma-Aldrich) and Ni(NO₃)₂·6H₂O (Alfa Aesar) solutions were infiltrated into the samples simultaneously (50%/50% by mass of Ni/Cu)/YSZ scaffold. The precursor solution for the Cu and Ni loadings were prepared by dissolving

nitrate salts in distilled water with a total metal concentration of 1 mol L⁻¹. After each infiltration step, the cells were heated to 350°C to decompose the nitrate species. The loading of the impregnated oxides was estimated by measuring the weight differences before and after each impregnation-heating treatment. The infiltration/calcination procedure was repeated up to the desired loading (50 wt% YSZ scaffold + 50 wt% anode material) with a 1:1 Cu:Ni mass ratio. After the final loading, the cells were calcined at 820°C for 2 hours. Two identical discs were prepared, and one of them was sealed into an alumina tube with an inner diameter of 1 cm using a zirconia-based adhesive (Aremco 885). The cell was placed in a split furnace (Lindberg) and heated to 820°C at a heating rate of 50°C h⁻¹. At 820°C, the cells were reduced with pure H₂ for 4 hours. Then, the reduced disc was carefully removed from the alumina tube, and the flaky parts of the reduced and non-reduced anode discs were scratched with a pin to obtain powder samples. X-ray diffraction analyses were performed on the obtained powders.

After examining the effect of the pore former and intra-cell interactions of Ni and Cu, a different cell preparation system was applied to Ni-interlayer-containing cells. In these structures, lamination was not used. The supports were obtained by sintering only the electrolyte films at 1600°C for 6 hours. The NiO/YSZ layers were applied by coating with a Ni ink using a simple spray gun. After NiO/YSZ coating, the bilayer structures were sintered for 6 hours at 1450°C. The composition of the Ni ink is given in Table 2. The thickness of the Ni layer was tailored by preliminary investigations of the coating process (the amount of sprayed ink to Ni-layer thickness relations). After sintering the Ni layers, for the second anode part, the pore former + YSZ-containing anode slurry was applied by brushing. Then, the dual layer anode was co-sintered at 1400°C for 6 hours.

TABLE 1 Tape-casting slurry composition for anode and electrolyte layers

	YSZ	Graphite	Potato Starch	PVA	Glycerol	PEG	Dispersant	Water
Anode	15	12	3	62.5	2.5	2.5	1	19
Electrolyte	30	-	-	62.5	2.5	2.5	1	19

PVA was used as %8 solution in DI-water. The water column corresponds the ball milled suspensions. The values describe gram amount of species.

TABLE 2 NiO spray ink composition for the NiO/YSZ interlayer

YSZ	NiO	Vulcan XC-72	Corn Starch	Polyvinyl Butyral	Dibutyl Phthalate	Menhaden Fish Oil	Acetone (1) / Ethanol(1)
5	5	4	1	5	3	2	75

The values describe gram amount of species.

After obtaining the porous YSZ layer + NiO-YSZ layer + dense YSZ layer, lanthanum strontium manganite (LSM) paste (NexTech Materials) was mixed with YSZ powders (50 wt% LSM + 50 wt% YSZ) and brushed on the other side of the electrolyte as the cathode layer and sintered at 1250°C for 3 hours. The composition of the cathode slurry is given in Table 3.

Then, the Cu-CeO₂ salt mixture was infiltrated into the structure at 30CeO₂/70 Cu ratio (details are given in our previous work³⁰). After each infiltration step, the cells were heated to 350°C to decompose the nitrate species. The infiltration/calcination procedure was repeated up to the desired loading (50 wt% YSZ scaffold + 50 wt% anode material). After the final loading, the cells were calcined at 820°C for 2 hours. All the loading steps were followed by the weighing of the cells with a precision scale.

Silver mesh, silver paste, and silver wire were applied to both sides of the cells as electrical contacts. Subsequently, the discs were sealed onto an alumina tube with an inner diameter of 1 cm using a zirconia-based adhesive (Aremco 885). The cells were placed in a split furnace (Lindberg) and were heated to 820°C at a heating rate of 50°C h⁻¹. At 820°C, the cells were reduced with pure H₂ for 4 hours and cooled to 800°C.

At this temperature, the current-voltage (*I-V*) characteristics of the cells were examined with recirculating air as the oxidant and pure, water-free H₂, and CH₄ as fuels. Figure 2 shows the preparation procedures followed for a single cell.

Subsequently, the size of the button cells was increased, and 4 home-made 5 cm × 5 cm cell structures were prepared. Reference cell selection and performance analysis were considered as criteria for the selection of the 4 cells. NiO/YSZ and CuO/CeO₂/YSZ were used as reference cells. Following cell performance analysis, 2 cells were chosen as the best performers, and their size was increased.

In the preparation of the 5 cm × 5 cm cells, the first step is the preparation and sintering of the electrolyte tapes. The content of the tape is the same as that of the disc cells. In this context, wide-area electrolyte films were cast by tape-casting. Electrolyte films of 6.67 cm × 6.67 cm area were cut and sintered at 1600°C for 6 hours.

For the preparation of the NiO/YSZ reference cell, a slurry containing 33 wt% NiO/33 wt% YSZ + 33 wt% pore former (graphite + potato starch) was prepared and applied by brushing. The anode layer was then sintered at 1450°C for 6 hours. For the CuO/CeO₂/YSZ cell, an

TABLE 3 Cathode slurry composition

YSZ	LSM	Graphite	Potato Starch	Polyvinyl Butyral	Dibutyl Phthalate	Menhaden Fish Oil	Acetone (1) / Ethanol(1)
10	10	8	2	10	6	4	50

The values describe gram amount of species.

Ni-interlayer containing single-cell preparation

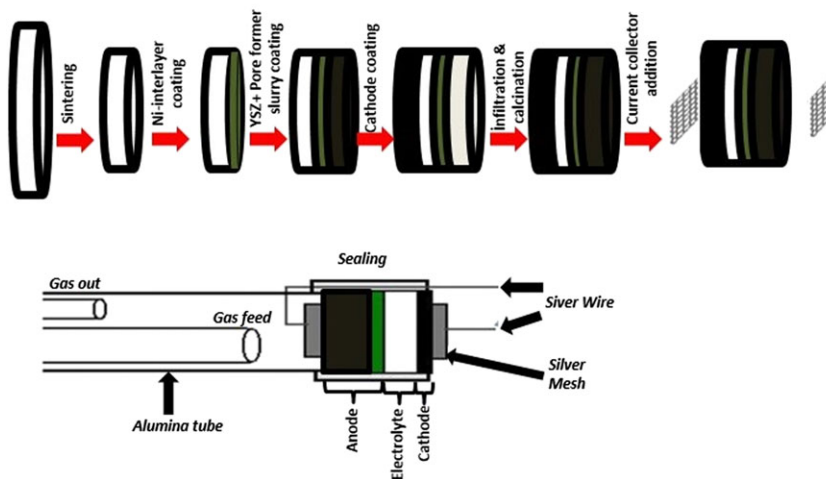


FIGURE 2 A diagram of button cell preparing procedure for NiO/YSZ interlayer containing anode structures [Colour figure can be viewed at wileyonlinelibrary.com]

anode slurry containing 50% pore former was applied to the dense electrolyte layer and sintered at 1400°C for 6 hours. The cathode material was applied by brush and sintered as for the button cells. The salts were then impregnated into the porous anode structure simultaneously at a 3:1 Cu:CeO₂ ratio.

Following the performance analysis, a dense electrolyte structure was prepared and coated with the NiO/YSZ target thickness to prepare the selected cells. The composition of the sprayed slurry is the same as described previously. A similar examination was carried out for the coating thickness and spray-ink quantity, and the appropriate amount of coating ink was applied on the 5 cm × 5 cm electrolyte in a 4 cm × 4 cm area. Then, a YSZ + pore former containing layer was applied to the half-cells, as in the disk cells, followed by sintering at 1400°C for 6 hours. Subsequently, the cathode was applied, and the Cu and CeO₂ salt solution was impregnated. The scaled-up cells were characterized using the established test system given in Figure 3.

The stability of the cells under direct CH₄ flow was examined after *I*-*V* measurements of the 4 cells. For this purpose, the current generated by the cells at constant voltage was monitored at the maximum power density and voltage. Therefore, the time-dependent cell stability was determined.

2.1 | Characterization

Thermogravimetric analysis (TGA, Seiko SII Exstar 6000) was used to reveal the thermal characteristics of the pore formers. The investigation was carried out from room temperature to 1000°C in an air atmosphere at a heating rate of 10°C min⁻¹.

Microstructural characterization of the study was performed using a scanning electron microscope (SEM,

FEI Quanta FEG 450). The samples to be inspected were affixed to double-sided copper tape. Powder samples (such as starch and activated carbon) were prepared by sprinkling the powder onto the tape.

When examining the cell structures, the discs were broken and stuck perpendicularly to the tape. To obtain SEM images, it was necessary to coat the insulator specimens with a conductive coating because of the working principle of the microscope. Thus, the samples were coated with Pd/Au, which is the most suitable coating. After coating, the samples were placed in the device, and microstructure studies were carried out at a voltage of 10 to 30 kV under a vacuum of less than 3×10^{-2} Pa. The anode compositions of the cells were also investigated using energy dispersive X-ray spectroscopy (EDS), which was used for line analysis and to identify the elemental distributions of Ni, Cu, and Ce in the depth profile of the anode.

X-ray diffraction pattern studies were carried out with RIGAKU D/max-2200 X-Ray diffractometer. The analyses were carried out at a scan rate of 2° min⁻¹ at 2 θ values from 20 to 90°. The obtained data were analyzed by means of pattern matching programs using XRD patterns from the Joint Committee on Powder Diffraction Standards (JCPDS). In this way, the pre/post-treatment behaviors were revealed.

Current-voltage measurements were carried out using a GAMRY-Reference 3000 pPotentiostat and a 3-30 booster system. The voltage was ramped from the open-circuit potential (OCV) to zero voltage at a rate of 5 mV s⁻¹ while measuring the voltage and current. The power densities of the samples were calculated using the universal relationship $P = IV$ based on the *I*-*V* curves. The stabilities of the 4 large cells were tested using chronoamperometry measurements.

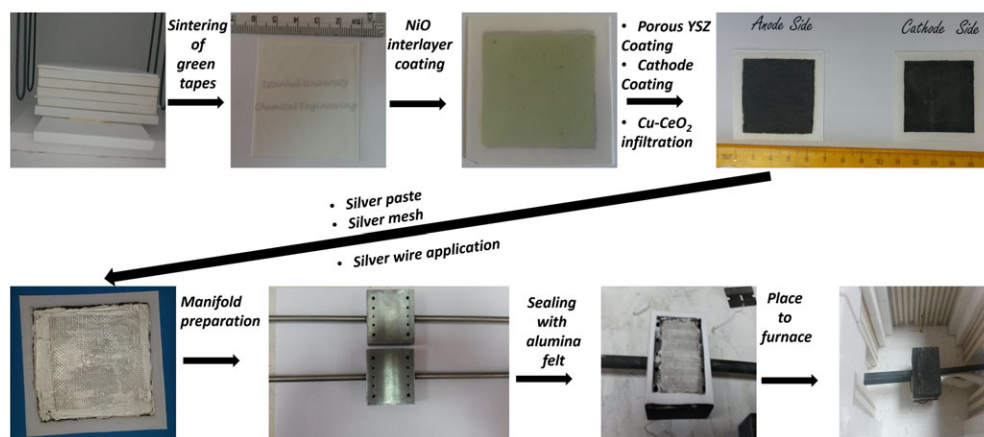


FIGURE 3 Flowsheet of 5 cm × 5 cm planar cell preparing procedure for NiO/YSZ interlayer containing anode structures [Colour figure can be viewed at wileyonlinelibrary.com]

3 | RESULTS AND DISCUSSION

3.1 | Pore former investigation

SEM images of the pore formers used in the study are shown in Figure 4A-D. As shown, the potato starch particles are globular and elliptical with diameters ranging from 10 to 100 μm . The tape thickness to be prepared with the large potato starch granules will be at least the size of the largest potato starch grain. The graphite (Figure 4B) particles have a lamellar structure in the range of 20 to 30 μm . We considered that this laminated structure would partially open during mixing to provide more effective porosity than the existing dry structure. As shown in the SEM image of activated carbon (Figure 4C), the particles are spherical and approximately 20 to 30 nm in size. The particles of cornstarch are around 5 to 10 μm in size, much smaller than the potato starch particles and with a narrower grain spacing.

SEM images of the samples after pore-former burn-out are shown in Figure 4E-H. In the potato starch-containing structure, the pores formed after sintering have a spherical structure, like dry starch, and the largest pores are approximately 25 to 30 μm in diameter, formed of circular cavities of different diameters. In addition, the remaining structure is very dense, despite its high porosity. Only pores in the macrostructure will cause a reduction in surface area. Hence, in the case of the catalyst loading in the later stages, the formation of a limited catalyst-YSZ interlayer for the formation of the TPB in which the reactions occur will be a problem. In the graphite-containing structure, the voids were found to have a rectangular structure of 15 to 25 $\mu\text{m} \times 5$ to 10 μm . Furthermore, the opening of the lamellar structure provides very small pores in the structure. In the

YSZ skeleton containing activated carbon, the pores are sub-micron sized. Pores of 5 to 6 μm were formed in the cornstarch.

The thermal behaviors of the 4 pore formers mentioned are shown in Figure 5. The decomposition of potato starch in the air started at around 320°C. In contrast, complete decomposition occurred at around 500°C to 550°C. The thermal behavior of the cornstarch is similar to that of potato starch. Only 5°C to 10°C differences were observed. The starch molecules consumed at low temperatures do not add micropores to the structure, except for the large pores. After the pore former is consumed, the structure will become open to sintering. As shown in the thermogram of graphite, the sample started to burn around at 650°C, whereas, in the case of single-stage decomposition, it has a total removal temperature of 850°C to 900°C. Hence, the sintering of the YSZ

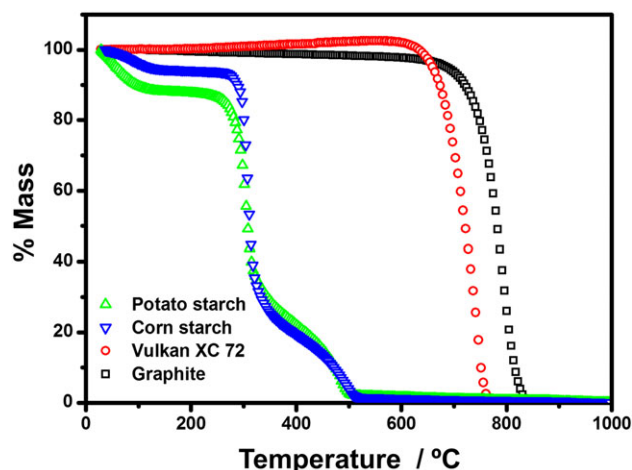


FIGURE 5 Temperature-dependent mass loss profiles for different pore formers under air flow condition [Colour figure can be viewed at wileyonlinelibrary.com]

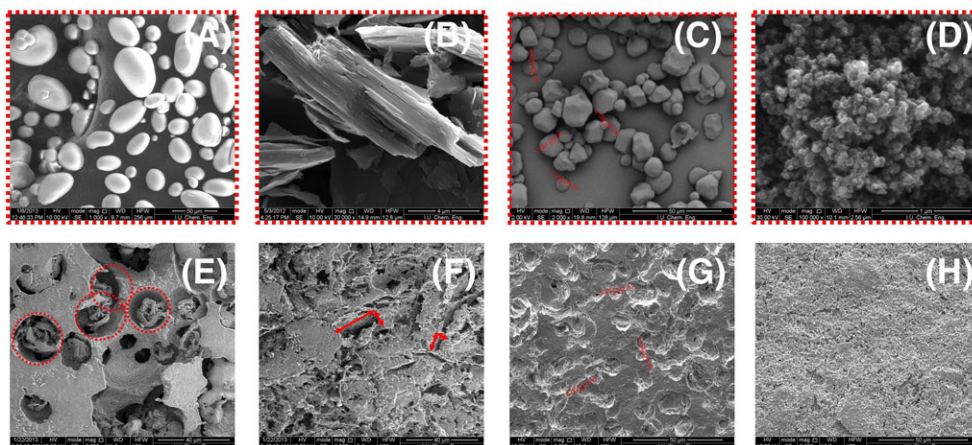


FIGURE 4 SEM images of different pore formers: A, potato starch, B, graphite, C, cornstarch, and D, vulkan XC-72. Cross-section SEM images of pore former burned out YSZ skeletons: E, potato starch, F, graphite, G, cornstarch, and H, vulkan XC-72 [Colour figure can be viewed at wileyonlinelibrary.com]

framework will be delayed to these temperatures. This will contribute not only to large pores in the construction, but also to a large surface area by providing small pores in the YSZ skeleton. The Vulcan XC-72 activated carbon behaved as a graphite nano-analog and the oxidation starting at 650°C was complete at 770°C to 800°C.

In this study, as described earlier, a dual-layer anode structure was prepared. Because both Cu and CeO₂ were applied to the anode skeleton after sintering, both large and small pores must be present in the structure. That is, both large and small pores are needed for the infiltration of Cu and Ce salts and to provide sufficient surface area.

Notably, graphite and potato starch cannot be used in the NiO/YSZ layer because of their large size and because the main aim of the study is to form a NiO/YSZ layer of ≤ 20 μm thickness. Considering the 30- μm pores formed by the oxidation of the 100- μm diameter potato starch particles and the 20- μm pores formed by graphite oxidation, the formation of a NiO/YSZ layer at the target thickness using these pore formers would be impossible. However, porosity is required for fuel diffusion to the interior of the TPB of the NiO/YSZ interlayer. Thus, activated carbon and cornstarch were used to form micropores in the NiO/YSZ interlayer. Graphite and starch were used to obtain higher porosity in the second layer coated on the NiO/YSZ.

3.2 | Ex situ XRD analysis to determine the Ni-Cu interactions

Figure 6 shows the XRD pattern for the Ni and Cu species impregnated into the anode skeleton. In the preparation of the cell, nickel nitrate hexahydrate and copper nitrate

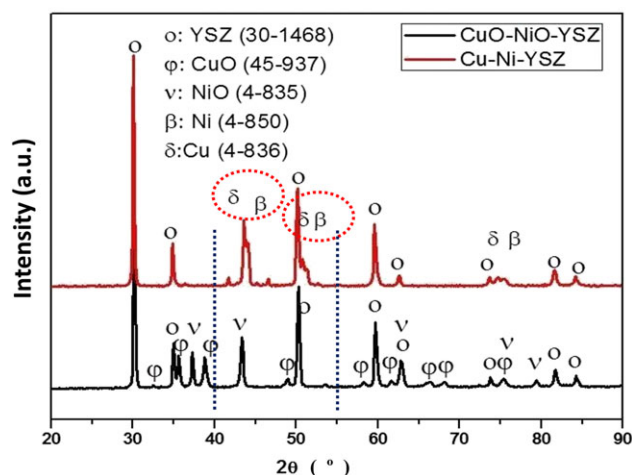


FIGURE 6 X-ray diffraction pattern of simultaneously infiltrated Ni and Cu before and after reduction with H₂ in YSZ scaffold. Black line refers to non-reduced, and red line refers reduced anode structure [Colour figure can be viewed at wileyonlinelibrary.com]

trihydrate salts were dissolved together in water at a mass ratio of 1:1, and simultaneous impregnation was carried out in 2 discs. After impregnation, calcination was carried out, and 1 disc was reduced at 820°C in pure hydrogen for 4 hours. The main reason for the ex situ instead of in situ evaluation of the cell containing the interlayer is because it is difficult to identify the interactions with Cu, which leaks into the thin Ni-interlayer. Thus, cell dissection was carried out because it is not possible to isolate the nickel-containing intermediate zone from the whole cell.

As can be seen, the characteristic peaks of CuO (JCPDS: 45-0937) and NiO (JCPDS: 04-0835) species in the unreduced sample are visible. When the XRD patterns of the Cu (04-0836) and Ni (04-0850) species are examined after reduction, 3 peaks at $2\theta = 44^\circ$, 51° , and 75° are in different positions from the peaks registered for the corresponding species.

Examining in detail the 40° to 54° region of the XRD patterns of the samples simultaneously impregnated with Ni and Cu and then reduced, as shown in Figure 7, it can be seen that both metals retain their characteristic peak positions, but the peaks are shifted toward those of the other species. However, in the case of bimetallic/alloy formation, the 2 metals behave as a single material, having patterns unlike those of the original structures, and it is known that the XRD pattern of a bimetallic material shows peak positions of a single species rather than 2 species.³¹ Thus, we estimated that 2 distinct solid solutions rich in both species had formed, as summarized in Figure 7.

That is, the Cu diffraction peaks shifted to higher 2θ positions than those of the pure state, indicating a Cu-rich Ni-Cu alloy, whereas the Ni diffraction peaks shifted to lower 2θ positions, indicating a Ni-rich Ni-Cu alloy. Thus, the formation of bimetallic species began after 4-hour reduction.

3.3 | SEM investigation of the NiO/YSZ interlayer

After discussing the pore-forming effect and the Ni-Cu interactions within the cell, we return to the layered anode structure, which is the main purpose of the work, and was first studied by Virkar et al.^{32,33} They found that the TPB regions within the anode are not present throughout the entire anode and are only present up to a certain distance from the electrolyte boundary. Thus, modifications were made to the NiO/YSZ anode structure to reduce the anodic polarization; for example, a highly porous support layer was prepared using coarse NiO grains to reduce the concentration polarization and to reduce the size of the electrolyte boundary. In addition, NiO grains were used to reduce the activation polarization.

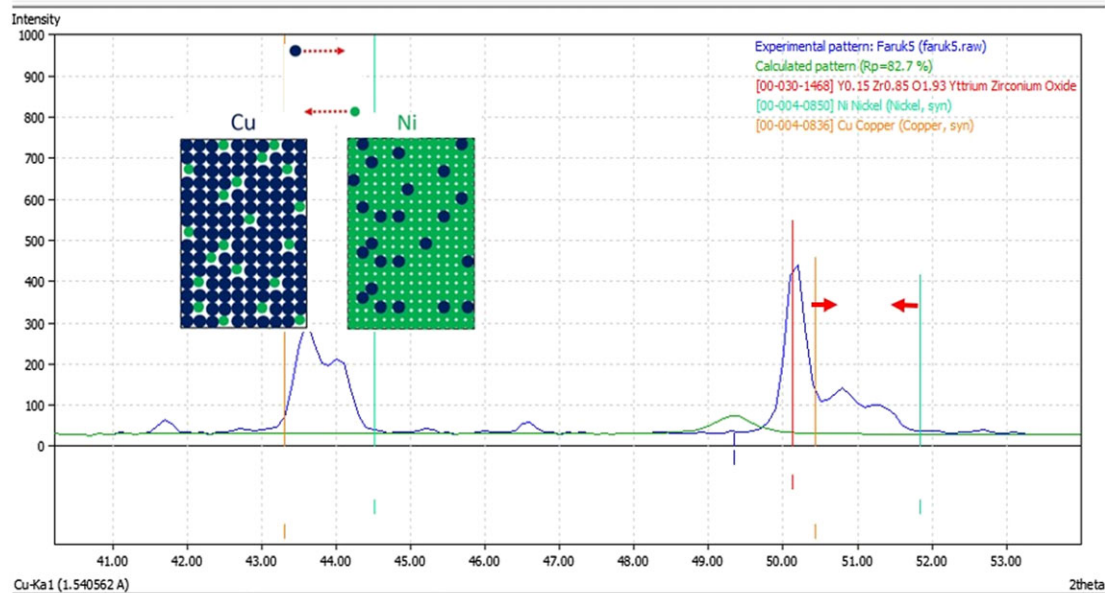


FIGURE 7 Detailed XRD pattern investigation for 40° to 54° for reduced Ni and Cu species [Colour figure can be viewed at wileyonlinelibrary.com]

Similarly, Chen et al³⁴ investigated the effects of porosity on the active layer. To do this, they did not use a pore former in the active layer, and different thicknesses of the active layer having a 60 wt% NiO/40 wt% YSZ composition were used. The support layer was very thick, and the cells contained less NiO than the active layer, using as little as half the NiO, to examine the gas permeation and cell performance. They found that, for anode functional layers (AFLs) with a thickness of 5 μm , the cell performance was improved with only 1 coating compared with the case without an AFL. In contrast, the cell performance with 2 and 3 coatings decreased. Therefore, there is an optimum AFL thickness.

Abudula et al³⁵ studied the mechanism of the oxidation reaction and the effective anode thickness of the anode structure. There was no gas phase oxygen in the anode, but they found that oxygen ions diffused from the electrolyte boundary to a certain depth. That is, the active region in the cell progresses from the point of contact with the electrolyte to a limited area. In their work, the anode thickness was varied from 17 to 140 μm , and the cell performances were examined. Effective TPB regions reaching 120 μm for hydrogen fuel are possible, whereas, in the case of methane fuel, this thickness is reported to be up to 70 μm .

In another study, Wang et al³⁶ prepared the support layer by the pressing-sintering method, followed by AFL application with the electrophoretic deposition technique, yielding a layer with 2.5 to 14- μm thicknesses. According to the results, they found the best performance in a structure containing a 10- μm -thick AFL. The reason for this result is that, above a certain AFL thickness, the

reactants cannot diffuse into the active sites and the product/reactant back diffusion is difficult.

Meng et al³⁷ studied the Cu-CeO₂ anode structure on a Ni/YSZ AFL in a tubular system and investigated the effect of the AFL thickness (13, 25, and 74 μm). Accordingly, they found the highest performance in the cell with the lowest thickness. The reason for this is that the thin AFL may have reduced the anodic polarization because of the easy gas and ion diffusion. In addition, carbonization did not occur over 85 hours of direct methane conversion with the 13- μm Ni/YSZ-containing anode structure, but, after 130 hours of the investigation, a small amount of carbonization occurred.

Finally, we summarize our past work,²⁵ where we obtained stable operation with the layered anode structure. We found that carbonization can be inhibited when the cracking catalyst in the cell is placed only in the near-electrolyte region, ie, oxygen-rich zones, where cell performance could be maintained.

In this work, a successful coating has been achieved by a simple ink-spraying method. The SEM and EDS line analysis of the samples, given in Figure 8, which contain the intermediate layer, reveal the coatings were very close to the target coating thickness after preparation with a very simple method. The coating thicknesses were 6.9, 11.5, 14.6, and 23.4 μm for the 40% NiO samples, 5.5, 12.4, 16.9, and 27.1 μm for the 50 wt% NiO samples, and 4.4, 10.3, and 15.7 μm for 60 wt% NiO samples compared with the target thicknesses of 5, 10, 15, and 20 μm , respectively. Unfortunately, SEM images could not be obtained for the 60 wt% NiO sample with the 20- μm target. In that case, the anode structure was completely

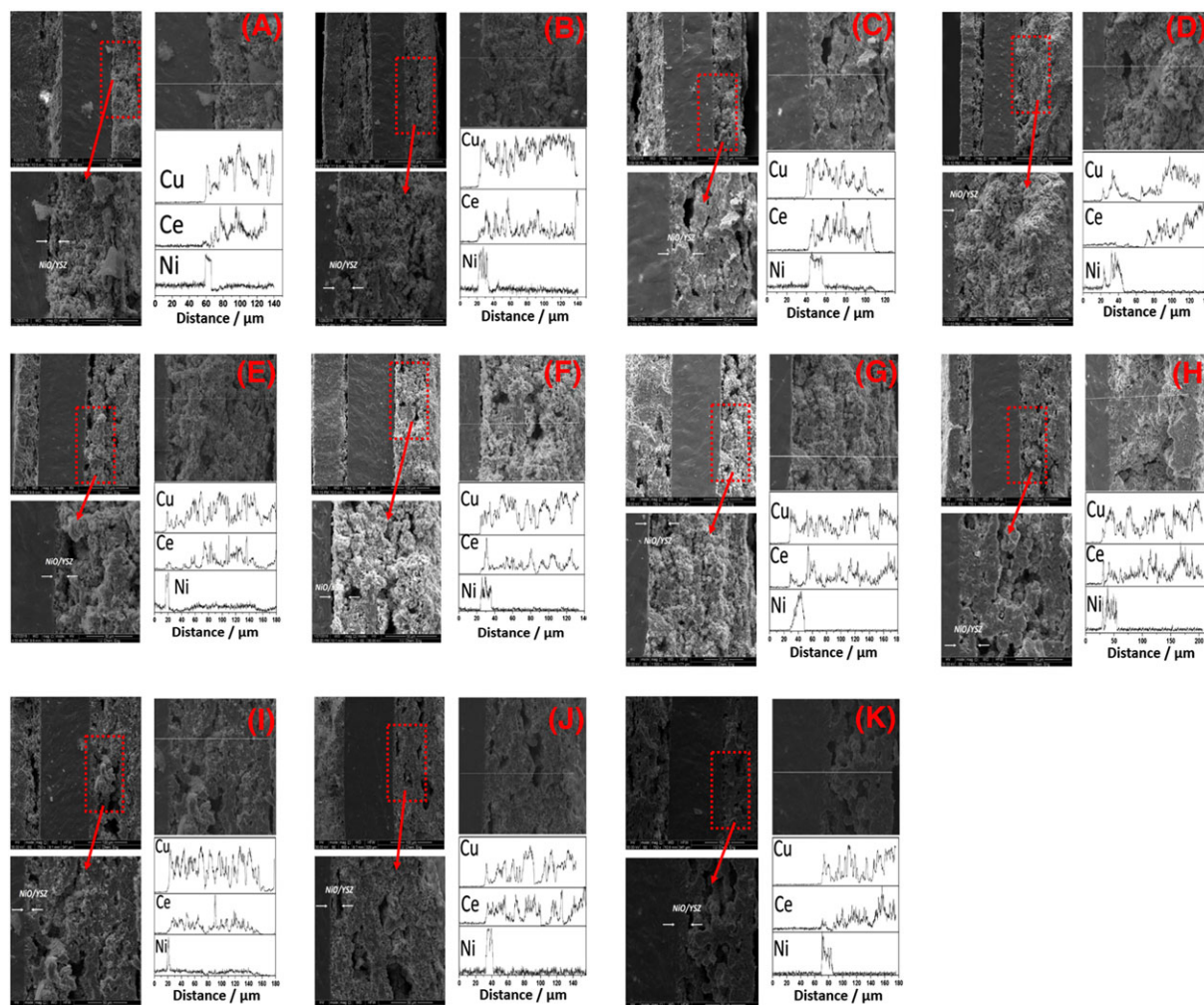


FIGURE 8 Cross-section SEM images and line-EDS elemental Ni, Cu, and Ce distribution images for A, 5 μm —40 wt% NiO, B, 10 μm —40 wt% NiO, C, 15 μm —40 wt% NiO, D, 20 μm —40 wt% NiO, E, 5 μm —50 wt% NiO, F, 10 μm —50 wt% NiO, G, 15 μm —50 wt% NiO, H, 20 μm —50 wt% NiO, I, 5 μm —60 wt% NiO, J, 10 μm —60 wt% NiO, K, 15 μm —60 wt% NiO, interlayer containing samples [Colour figure can be viewed at wileyonlinelibrary.com]

deformed during the separation from the alumina tube, and SEM examination was not performed.

In addition, in the SEM images of all the cells, the electrolyte layer was observed to be very dense, and good sintering was observed. The electrolyte thicknesses were in a narrow range of 120 to 130 μm . The similar thickness values of the structures prepared by cutting from the same film indicate that the tape-casting process was also very successful.

The microstructure has a significant effect on the cell performance. The high density of the electrolyte layer contributes to increasing the ionic conductivity by reducing the grain boundary resistance for ion transport. In addition, the lack of the open pores of the electrolyte is also very important in terms of the molecular oxygen inflow to the anode side from the cathode because the oxygen partial pressure in the anode compartment will cause a decrease in the OCV of the cell.³⁸ In addition,

the intermediate NiO/YSZ layer on the YSZ electrolyte was very compatible with the electrolyte, and the porous YSZ skeleton showed good adhesion to both layers.

The porosities of the button cells were measured via hot water soaking capacities³⁹ of cathode uncoated half-cells. This ex-situ examination was carried to reveal the individual porosity of the anode structure because of general cell preparation procedure; the cathode coating was done before CuO/CeO₂ loading. The overall anode porosities were calculated around 55% to 60% by volume before CuO/CeO₂ loading, and after loading the anode porosity of the half-cells reduces to around 30%. This value is similar with the work done by Meng et al.⁴⁰ and sufficient for the requirement of as an anode of SOFC.⁴¹

In these structures, morphological differences could hardly be detected, and thickness determination could only be demonstrated by sensitive elemental analysis such as EDS. Because Cu and CeO₂ are subsequently

filled into the structure and penetrate most regions, a similar morphology to that of the original is formed. However, the AFL layers have lower porosity because of the pore former used; that is, activated carbon and corn-starch were used to achieve porosity in the interlayer, whereas graphite and potato starch were used in the second layer where Cu and Ce are loaded.

In addition, when the EDS line results are examined, it can be seen that the distribution of Cu and Ce was effectively distributed in the Ni-containing regions. In this case, the TPB regions in the nickel region were activated by the Ni-Cu contacts, and the Cu-CeO₂ performance contribution was achieved in the nickel-free regions. In terms of electrical percolation, the NiO region must be somehow connected to the current collecting silver wire. This connection can only be achieved by providing a Cu current flow path that is in direct contact with the Ni-region. For this reason, Cu infiltration into the interlayer is vital in terms of cell performance.

CeO₂ leakage into the AFL can be considered as introducing the co-catalyst into the reaction zone in an oxygen-rich region, while Cu presence in this region will have a different effect. The leakage of Cu into the AFL, which is the bridge between the AFL and the current collector, increases the potential TPBs in the AFL. However, as we have shown, the formation of the Ni-Cu bimetallic phase has advantages and disadvantages. For example, bimetallic species formation increases the resistance to carbonization⁴²⁻⁴⁴ but reduces the ability of nickel to dissociate methane,⁴⁵ resulting in decreased catalytic activity.

3.4 | Performance analysis of the button cells

Figure 9 shows the results of current-voltage tests at 800°C for H₂ and CH₄ for the button cells.

The open circuit voltage values in the cells vary between 1000 and 1100 mV. These results are consistent with the thermodynamic calculations of the system and the reported values.⁴⁶ In addition, the high OCV values also indicate dense electrolyte structures, as discussed in the SEM investigation. Next, the power densities of the cells were investigated. In the case of 40 wt% NiO at 800°C, the maximum power densities were found to be 182, 204, 231, and 241 mW cm⁻² for CH₄ and 224, 254, 277, and 281 mWcm⁻² for H₂ fuel for the 5, 10, 15, and 20 μm NiO/YSZ interlayer cells, respectively. On increasing NiO content to 50 wt% at 800°C, the maximum power densities of the cells were found to be 198, 216, 227, and 234 mWcm⁻² for CH₄ and 251, 269, 283, and 273 mWcm⁻² for H₂ fuel for the 5, 10, 15, and 20 μm NiO/YSZ interlayer cells, respectively. For the 60 wt% NiO cell

at 800°C, the maximum power density values of the cells were found to be 163, 179, 187, and 204 mWcm⁻² for CH₄ and 197, 216, 221, and 236 mWcm⁻² for H₂ fuel for the 5, 10, 15, and 20 μm NiO/YSZ interlayer cells, respectively.

Figure 10 summarizes the relationship between the NiO/YSZ interlayer thickness and maximum power densities measured from the related cells.

For the 0-μm thickness shown in Figure 10, the data were obtained from a sample with an anode structure containing only Cu-CeO₂-YSZ and no Ni-interlayer, as reported in our previous work.³⁰ When the results were examined, we found that the power densities tended to be fixed at a certain point in almost all cases. Even in the case of H₂ fuel, a decrease in the power density of the 20/50 (where 20 indicates 20-μm thickness and 50 indicates 50 wt% NiO) cell compared with the 15/50 and 20/40 cells was observed. The performance of the 50 wt%-series samples was exceeded by the 40 wt%-series for H₂ fuel with a 17-μm-thick layer NiO/YSZ and for CH₄ fuel with a 14-μm-thick layer NiO/YSZ. Although a continuous increase in power density was observed in the 60%-series samples, these values are considerably lower than in the 40 wt%-series and 50 wt%-series samples. Kagomiya et al⁴⁷ reported that increasing the AFL layer thickness results in concentration polarization because the AFL layer is denser. In addition, for high NiO contents, Hassan et al⁴⁸ stated that the presence of excess NiO might cause a thermal expansion mismatch and nickel agglomeration and, thus, a performance decrease. In addition, they found that the 40 wt% NiO containing state was the best cell structure. In the same study, although the performance was not significantly affected by the thickness of the active layer up to 8 μm, the performance decreased as the thickness increased to 16 μm. The cell performance is directly related to the active sites and the number of TPBs.

In studies that investigated the TPB concentration in the AFL anode, statistical analysis of the reaction zone using focused ion beam-SEM has provided useful results.⁴⁹ In this regard, Wilson et al⁵⁰ studied the phase continuities in the anode structure. A total volume of 110 μm³ and approximately 10 μm thickness of the active layer was mapped by analyzing 82 slices, and a 3-dimensional Ni-YSZ distribution was calculated. According to this analysis, after reduction, the percolation in the YSZ is 100%, although there was a 13% interruption in NiO, and 1.5% isolated Ni particles were observed. In their study, the use of a higher amount of NiO to reduce these discontinuities was disputed. Similarly, Wilson et al stated that ion transport is more vital for the cell and that cells that suffer from interruptions in the YSZ cannot be accepted because the rate determining part of the cell is the electrolyte. In another study,⁵¹ the same group

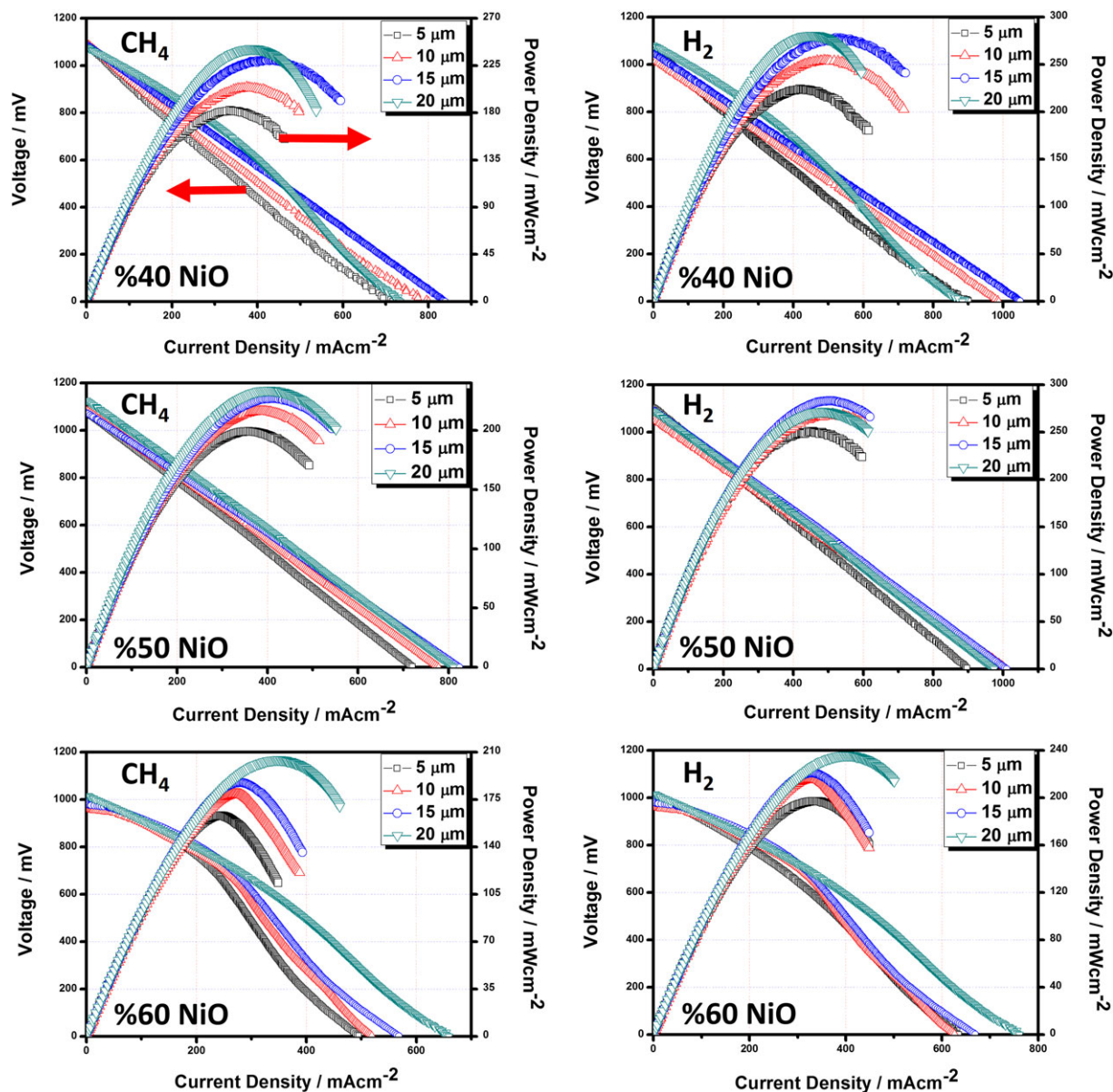


FIGURE 9 The potential and power density versus current densities of the button cells. Performance comparisons of the cells for different NiO content and NiO/YSZ thickness at 800°C, for methane and hydrogen fuels [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

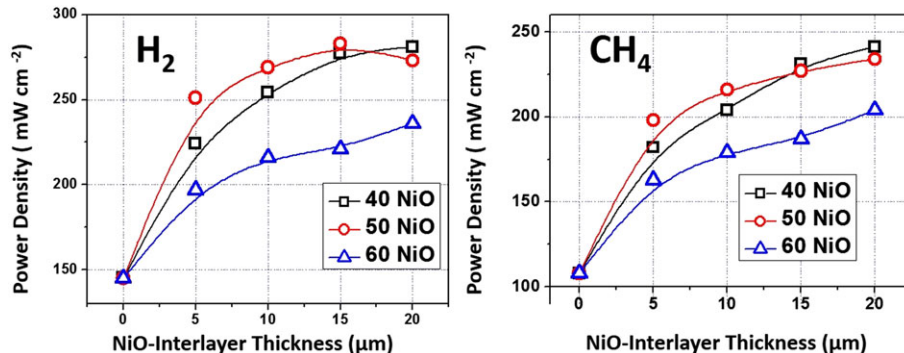


FIGURE 10 Summarized power density-NiO/YSZ thickness results for button cells [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

reported that the most suitable NiO/YSZ ratio in terms of TPB formation was approximately 50% based on their stereological analysis. In another study,⁵² it was reported

that the electrochemical active TPB concentration was the highest for a 50 wt% NiO-50 wt% YSZ state when 40 wt%, 50 wt%, 60 wt%, and 70 wt% NiO were compared.

In another study, Vivet et al.⁵³ performed a high-level analysis based on Wilson's study and found a percolation threshold with approximately 55 wt% NiO + 45 wt% YSZ in a 1000- μm^3 sample. Accordingly, they found that the TPB depth in the anode was approximately 7.4 μm . Then, in a second paper,⁵⁴ they studied the ratio of Ni/YSZ in terms of percolation and electrochemical activity. They prepared cermet constructions containing 44 wt%, 51 wt%, 54 wt%, 56 wt%, and 61 wt% NiO and found that Ni-percolation was not achieved until a mass of 54% NiO was used, resulting in 88% percolation for 54 wt% NiO and approximately 97% percolation for 61 wt% NiO. Nevertheless, they pointed out that the highest specific YSZ-Ni interface area was 44 wt%, which has the lowest Ni content. It was also found that the highest surface area to nickel ratio was achieved at 44 wt% NiO because the use of excessive NiO causes agglomeration. Finally, they determined that the specific interface length of the TPB_L is achieved with a 40 wt% NiO/60 wt% YSZ structure.

The work of Vivet is particularly important because it makes sense that a decrease in the Ni ratio “increases the number of potential reaction sites” if “electrical percolation is provided.” This suggests that the Ni-YSZ specific interface increases, but the corresponding regions are inactive TPBs because of electrical isolation. In Vivet's work, “one of the requirements for TPB formation” is not the nickel continuity but the continuity of the electrical conductor species. In this context, the inactive Ni-YSZ interface can be activated by contact with a percolated electrical conductor (copper). That is, while the Ni/YSZ interface increases with decreasing Ni ratio, the passive Ni-YSZ areas are activated by Cu introduced into the system as the conductive species. Thus, cell performance can be increased with a reduced nickel ratio.

The results of this study show that there is almost no difference between the 50 wt%-series and the 40 wt%-series, and both series performed better than the 60 wt%-series samples. In contrast, based on the focused ion beam-SEM studies, it is possible that there are no active TPBs in the cells because, in those studies, Ni-continuity was not achieved at 40 to 50 wt% NiO mass ratios. However, in our work, active areas were achieved when using nickel at low ratios with the help of copper. In other words, there are 2 different explanations for the lower performance in the 60 wt%-series samples. One explanation is nickel agglomeration and the second is the excess nickel, which can prevent YSZ percolation. As mentioned, both situations are possible.

Relevant to the AFL thickness investigation, the application of the AFL does not positively affect the performance above a certain thickness because of competition effects, which increase the concentration polarization and reduce the activation polarization. In

addition, it is very important to reduce the nickel content while improving the performance because the main goal of this study is to work directly with methane, and nickel is an excellent cracking catalyst. In particular, nickel particles that do not form TPBs (isolated or interrupted nickel) will support only the cracking reaction inside the cell. A similar situation occurs in areas where carbonization is more effective than oxidation.

Thus, when analyzing the performance increases in cells using methane fuel, the performance increase in the 40 wt%-series samples is 65% with a 0 to 5- μm layer thickness, 13% with a 5 to 10- μm layer, 12% with a 10 to 15- μm layer, and approximately 4% for the 15 to 20- μm layer. For the 50 wt%-series samples, the performance increase is 82% with a 0 to 5- μm layer thickness, 9% with a 5 to 10- μm layer, 5% with a 10 to 15- μm layer, and 3% with a 15 to 20 μm layer. Because the 60 wt%-series samples showed lower performance than the 40 wt%-series and 50 wt%-series samples at all thicknesses and percentages, they were not evaluated further.

3.5 | Scale-up and stability investigation for selected cells

When evaluating the available data, cell sizes of 5 cm $\times$ 5 cm were found to be suitable for the 15/40 and 15/50 samples, where the performance gain was very low at higher thicknesses. Because the effective TPB areas of these thicknesses were likely to decrease considerably, the relevant areas would only support carbonization. Thus, the scale was increased for the 2 selected cells. In addition, conventional Ni/YSZ and Cu/CeO₂/YSZ cells were prepared in large sizes to act as a reference cells. The current and power density results for the prepared 5 cm $\times$ 5 cm samples are given in Figure 11.

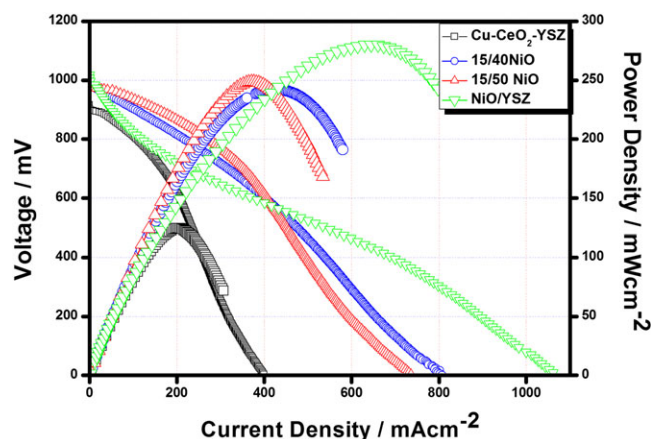


FIGURE 11 The potential and power density versus current densities of the planar cells for methane fuel at 800°C [Colour figure can be viewed at wileyonlinelibrary.com]

Compared with the button cells, performance improvement was observed in all of these samples. The performance increased by 13.7% for the Cu-CeO₂ cell, 4.7% for the 15/40 cell, and 13.2% for the 15/50 cell. It is thought that this is a result of gas diffusion at the points of contact with the alumina pipe during the preparation of the disk cells. Because, in these samples, the total surface area is 0.785 cm² in the case of Ø 1 cm, this value was taken as the active area. However, in the 5 cm × 5 cm specimens, there are no contact point problems, and the active area was 4 cm × 4 cm for the cells. Because of the low surface area in the disc cells, the effect of the small inactive regions originating from the preparation conditions is large, and this is believed to be the reason for the increased performance of the enlarged cells.

When the curves are examined in detail for the 15/50 and 15/40 samples, the 15/50 cell initially provided higher current values, but, in the low voltage region, the situation was reversed, and the 15/40 example was better in terms of the maximum current. The 15/50 cells showed lower activation polarization, whereas the 15/40 example showed lower concentration polarization. In addition, the reference cell containing NiO at a ratio of 50 wt% throughout the whole cell was the best cell in terms of performance. In contrast, the reference Cu-CeO₂-YSZ cell far behind others. Because of the study aims, if a comparison is made for CH₄ fuel, only 91.4% and 86.1% of the reference cell NiO/YSZ could be reached in terms of power density for 15/50 and 15/40 cells, respectively. Neither model cell achieved results better than the conventional NiO/YSZ cell. It is estimated that the reason for this is the formation of the Ni-Cu bimetallic species mentioned in the XRD evaluation. The activity of the Cu-rich and Ni-rich bimetallic species, even in the cell reduction step, was below that of Ni alone. Furthermore, as Cu was enriched in the alloy structure, its activity for methane dissociation decreased. Because of the bimetallic structure formed, it is not possible to achieve the sample performance as the conventional NiO cell. In this respect, the ratio of nickel in the nickel-rich alloy to be formed in the 15/50 cell will be higher than in the 15/40 cell. From this point of view, the 5% performance margin of 15/50 is understandable.

However, if our target cells are able to maintain stability in long-term operation, even though they do not provide superior baseline activity, they could be acceptable. Furthermore, it is necessary to consider all potential causes of degradation that may occur in long-term cell evaluation. In the cells, in addition to carbonization, Ni-Ni, Ni-Cu, or Cu-Cu contact breaks, nickel or copper agglomeration, a reduction in porosity, electrolyte delamination, and phase transitions are possible degradation pathways.

The long-term stability behavior of the 4 cells is shown in Figure 12. It is seen that only the nickel-

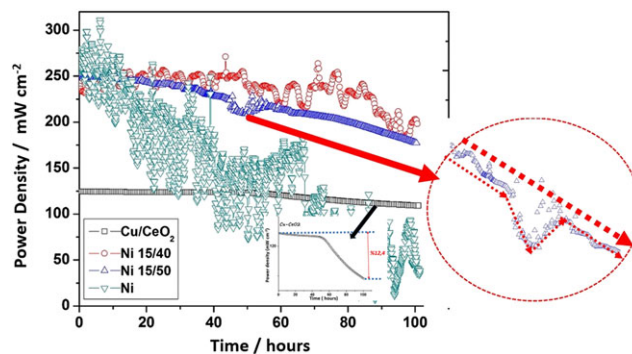


FIGURE 12 Plots of power density as a function of time (chronoamperometry) at 800°C for Ni/YSZ, Cu-CeO₂/YSZ, 15 μm/40 wt% and 15 μm/50 wt% NiO/YSZ interlayer containing planar cells. The fuel was pure CH₄, and the cell potential was maintained at different constant voltage [Colour figure can be viewed at wileyonlinelibrary.com]

containing cell began to deactivate from the first hour, probably because of carbonization, although a continuous oscillation was encountered. This oscillation arises because, at certain intervals, carbonization added conductivity to the cell, leading to an increase in instantaneous performance⁵⁵; however, the long-term behavior the cell suffered because of the carbonization. For the Cu-CeO₂ cell, initially, stable performance was observed. However, as time passed, the apparent performance loss, which started after 48 hours, increased, reaching 87.6% after 100 hours. Sintering occurred because of the low melting temperature of metallic Cu.⁵⁶

NiO-interlayered cells were run in parallel for a single NiO/YSZ-cell. Accordingly, performance decreases and sequential increases were observed. In particular, it is thought that 3 different mechanisms were effective in these cells:

- Sintering (especially for Cu-CeO₂).
- Bimetallic Ni-Cu single phase formation.
- Carbonization.

Although 2 kinds of metal-rich phases were found in the initial phase in the XRD analysis, long-term operation converts the single-phase structure into a 50/50 Cu-Ni structure. Therefore, in long-term operation, the activity changed in the cells until a single-phase structure was formed. The phase change is advantageous in terms of carbonization, but it has a negative effect on performance. In addition, the resulting alloy structure adds thermal stability to the Cu, but this is only of concern to the AFL. Therefore, the Cu-sintering of the AFL results in a loss of Cu-Cu contact points.

We evaluated the cells individually. In the 5 cm × 5 cm-15/50 cell, there was an increase in intensity

and slope of the performance degradation at around 45 hours. The cell then normalized and returned to baseline degradation performance. This was probably due to reactivation of the reaction centers related to the oxidation surface covered in carbon.

At this point, the rapid decline ceased, and the performance continued to decline slowly. The deactivation zone was considered to be the main cause of the revival of the nickel, which was active for the cracking reaction, in the oxygen-rich region. That is, we can refer to the “*self-regeneration of a locally carbonized region*.”

Despite the carbonization mechanism is still not fully understood,⁵⁷ it is known that the removal of deposited carbon depends on the local microenvironment of the anode.⁵⁸ The ease of removal follows the sequence of TPB > YSZ > Ni surfaces⁵⁹ due to the accessibility of the oxygen ions which is close to the electrolyte. Thus, the removal of deposited carbon allows the regeneration of the active sites and enhances the cell performance.⁶⁰

The main purpose of our study was to prepare structures that could completely resist carbonization in this region. However, although the cell was able to respond to the sudden loss in performance after 45 hours, it could not prevent performance loss in the long term. A performance loss of approximately 28.9% was observed after 100 hours, which was set as the target in the study, compared with the initial value.

In the 5 cm × 5 cm-15/40 cell, severe oscillatory behavior was observed. If the cell continued the behavior of the first hour, the cell would be completely deactivated after approximately 14 hours. However, with the response from the oxygen-rich area, it regained the initial value, and the power intensity even increased. In other words, we believe that the oscillations that occur in the cell were the result of the action-reaction behavior. As the surfaces were deactivated, performance degradation was observed. O²⁻, which is abundant in this region, was reactivated by the oxidation of C on the surface. Similar to the 5 cm × 5 cm-15/40 example, it was possible to obtain instant responses, but the loss of active sites, in the long term, cannot be prevented, resulting in a performance loss of approximately 18.3% of the initial value of the cell.

However, it is clear that the permanent loss of performance of 28.9% and 18.3% is not solely due to carbonization. As noted previously, the reference Cu-CeO₂ cell showed a 12.4% performance loss because of sintering. In addition, performance degradation because the nickel to nickel-copper alloy phase change should be considered. If a correction is made in the 15/40 and 15/50 cells for the sintering-induced performance drop of 12.4% observed in Cu-CeO₂, regardless of the phase change induced loss, it can be assumed that the performance

losses of 16.5% for the 15/50 cell and 5.9% for the 15/40 cell are due to carbonization.

The need for extensive work on the sintering problem is evident because, in this study, the carbonization-induced performance decline in the 15/40 cell was found to be lower than sintering-induced performance degradation.

We concluded that all the evaluations indicated that the CuO/CeO₂/YSZ-NiO/YSZ dual layer anode structure contributed significantly to improved cell performance showed reduced carbonization deactivation, and the best performing cells could compete with the conventional NiO/YSZ anode structure.

4 | CONCLUSION

The results of the study are as follows.

- It has been found that the frequently used pore formers, potato starch and graphite, are not suitable for electrode preparation at low thicknesses. Pore formers such as very fine activated carbon, cornstarch, and rice starch can be used. We found that, instead of the use of single pore former, the use of a mixture of multiple pore formers is appropriate.
- XRD studies showed that all Cu and Ni were reduced to metallic species in 4 hours. Simultaneous reduction of Ni and Cu in the cell environment resulted in 2 distinct copper-rich and nickel-rich bimetallic phases with their XRD peak coming close to each other. Thus, a single-phase bimetallic structure will be formed in long-term operation.
- Using a simple spray gun, cells can be prepared at controllable thicknesses and with desired properties.
- Increasing the NiO/YSZ interlayer thickness resulted in a slight increase in performance, but the performance dropped above the critical thickness.
- Although the content of nickel was higher in the 60 wt%-series cells than in 50 wt%-series and 40 wt%-series cells, the performance decline was possibly due to nickel agglomeration due to excess metal.
- For the 50 wt%-series and 40 wt%-series samples, the most suitable structure was that with a 15-μm-thick NiO/YSZ layer.
- In the long-term stability study, we found an inevitable 20 to 30 wt% performance loss.

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REFERENCES

1. Stambouli AZ, Traversa E. Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy. *Renew Sustain Energy Rev.* 2002;6(5):433-455.
2. Singhal SC. Advances in solid oxide fuel cell technology. *Solid State Ion.* 2000;135(1):305-313.
3. Ormerod RM. Solid oxide fuel cells. *Chem Soc Rev.* 2003;32(1):17-28.
4. Park S, Vohs JM, Gorte RJ. Direct oxidation of hydrocarbons in a solid-oxide fuel cell. *Nature.* 2000;404(6775):265-267.
5. Holladay JD, Hu J, King DL, Wang Y. An overview of hydrogen production technologies. *Catal Today.* 2009;139(4):244-260.
6. Ahmed S, Krumpelt M. Hydrogen from hydrocarbon fuels for fuel cells. *Int J Hydrogen Energ.* 2001;26(4):291-301.
7. Ni M, Leung DY, Leung MK, Sumathy K. An overview of hydrogen production from biomass. *Fuel Process Technol.* 2006;87(5):461-472.
8. Ge XM, Chan SH, Liu QL, Sun Q. Solid oxide fuel cell anode materials for direct hydrocarbon utilization. *Advanced Energy Materials.* 2012;2(10):1156-1181.
9. Murray EP, Tsai T, Barnett SA. A direct-methane fuel cell with a ceria-based anode. *Nature.* 1999;400(6745):649-651.
10. Atkinson A, Barnett SA, Gorte RJ, et al. Advanced anodes for high-temperature fuel cells. *Nat Mater.* 2004;3(1):17-27.
11. Lin Y, Zhan Z, Liu J, Barnett SA. Direct operation of solid oxide fuel cells with methane fuel. *Solid State Ion.* 2005;176(23):1827-1835.
12. Liu J, Barnett SA. Operation of anode-supported solid oxide fuel cells on methane and natural gas. *Solid State Ion.* 2003;158(1):11-16.
13. Finnerty CM, Coe NJ, Cunningham RH, Ormerod RM. Carbon formation on and deactivation of nickel-based/zirconia anodes in solid oxide fuel cells running on methane. *Catal Today.* 1998;46(2):137-145.
14. He H, Vohs JM, Gorte RJ. Effect of synthesis conditions on the performance of Cu-CeO₂-YSZ anodes in SOFCs. *J Electrochem Soc.* 2003;150(11):A1470-A1475.
15. Lee SI, Vohs JM, Gorte JRA. Study of SOFC anodes based on Cu-Ni and Cu-Co bimetallics in CeO₂ YSZ. *J Electrochem Soc.* 2004;151(9):A1319-A1323.
16. Gorte RJ, Kim H, Vohs JM. Novel SOFC anodes for the direct electrochemical oxidation of hydrocarbon. *J Power Sources.* 2002;106(1):10-15.
17. Huang YH, Dass RI, Xing ZL, Goodenough JB. Double perovskites as anode materials for solid-oxide fuel cells. *Science.* 2006;312(5771):254-257.
18. Tao S, Irvine JTS. Synthesis and Characterization of (La_{0.75}Sr_{0.25})Cr_{0.5}Mn_{0.5}O_{3-δ} a redox-stable, efficient perovskite anode for SOFCs. *J Electrochem Soc.* 2004;151(2):A252-A259.
19. Jardiel T, Caldes MT, Moser F, Hamon J, Gauthier G, Joubert O. New SOFC electrode materials: the Ni-substituted LSCM-based compounds (La_{0.75}Sr_{0.25})(Cr_{0.5}Mn_{0.5-x}Ni_x)O_{3-δ} and (La_{0.75}Sr_{0.25})(Cr_{0.5-x}Ni_xMn_{0.5})O_{3-δ}. *Solid State Ion.* 2010;181(19):894-901.
20. Gross MD, Vohs JM, Gorte RJ. An examination of SOFC anode functional layers based on ceria in YSZ. *J Electrochem Soc.* 2007;154(7):B694-B699.
21. Wang Z, Zhang N, Qiao J, Sun K, Xu P. Improved SOFC performance with continuously graded anode functional layer. *Electrochem Commun.* 2009;11(6):1120-1123.
22. Moon H, Kim SD, Park EW, Hyun SH, Kim HS. Characteristics of SOFC single cells with anode active layer via tape casting and co-firing. *Int J Hydrogen Energ.* 2008;33(11):2826-2833.
23. Tanner CW, Fung KZ, Virkar AV. The effect of porous composite electrode structure on solid oxide fuel cell performance I. Theoretical analysis. *J Electrochem Soc.* 1997;144(1):21-30.
24. Sariboğa V, Öksüzömer F. The investigation of active Ni/YSZ interlayer for Cu-based direct-methane solid oxide fuel cells. *Appl Energ.* 2012;93:707-721.
25. Meng X, Gong X, Yang N, Yin Y, Tan X, Ma ZF. Carbon-resistant Ni-YSZ/Cu-CeO₂-YSZ dual-layer hollow fiber anode for micro tubular solid oxide fuel cell. *Int J Hydrogen Energ.* 2014;39(8):3879-3886.
26. Meng XX, Gong X, Yang NT, Tan XY, Ma ZF. Preparation and properties of direct-methane solid oxide fuel cell based on a graded Cu-CeO₂-Ni-YSZ composite anode. *Acta Phys-Chim Sin.* 2013;29(8):1719-1726.
27. Li W, Guan B, Liu M, et al. On the limiting factor of impregnation methods for developing Cu/CeO₂ anodes for solid oxide fuel cells. *J Solid State Electrochem.* 2018;1-9.
28. Hornés A, Escudero MJ, Daza L, Martínez-Arias A. Electrochemical performance of a solid oxide fuel cell with an anode based on Cu-Ni/CeO₂ for methane direct oxidation. *J Power Sources.* 2014;249:520-526.
29. Liu M, Wang S, Chen T, et al. Performance of the nano-structured Cu-Ni (alloy)-CeO₂ anode for solid oxide fuel cells. *J Power Sources.* 2015;274:730-735.
30. Sariboğa V, Öksüzömer MAF. Cu-CeO₂ anodes for solid oxide fuel cells: determination of infiltration characteristics. *J Alloy Compd.* 2016;688:323-331.
31. Hornés A, Gamarra D, Munuera G, Conesa JC, Martínez-Arias A. Catalytic properties of monometallic copper and bimetallic copper-nickel systems combined with ceria and Ce-X (X= Gd, Tb) mixed oxides applicable as SOFC anodes for direct oxidation of methane. *J Power Sources.* 2007;169(1):9-16.
32. Kim JW, Virkar AV, Fung KZ, Mehta K, Singhal SC. Polarization effects in intermediate temperature, anode-supported solid oxide fuel cells. *J Electrochem Soc.* 1999;146(1):69-78.
33. Virkar AV, Chen J, Tanner CW, Kim JW. The role of electrode microstructure on activation and concentration polarizations in solid oxide fuel cells. *Solid State Ion.* 2000;131(1):189-198.
34. Chen K, Chen X, Lü Z, Ai N, Huang X, Su W. Performance of an anode-supported SOFC with anode functional layers. *Electrochim Acta.* 2008;53(27):7825-7830.

35. Abudula A, Ihara M, Komiyama H, Yamada K. Oxidation mechanism and effective anode thickness of SOFC for dry methane fuel. *Solid State Ion.* 1996;86:1203-1209.
36. Wang Z, Zhang N, Qiao J, Sun K, Xu P. Improved SOFC performance with continuously graded anode functional layer. *Electrochem Commun.* 2009;11(6):1120-1123.
37. Meng X, Gong X, Yin Y, Yang N, Tan X, Ma ZF. Effect of the co-spun anode functional layer on the performance of the direct-methane microtubular solid oxide fuel cells. *J Power Sources.* 2014;247:587-593.
38. Bürgler BE 2006, Single chamber solid oxide fuel cells, PhD thesis, Swiss Federal Institute of Technology, Zürich.
39. Boaro M, Vohs JM, Gorte RJ. Synthesis of highly porous yttria-stabilized zirconia by tape-casting methods. *J Am Ceram Soc.* 2003;86(3):395-400.
40. Meng X, Yan W, Yang N, Tan X, Liu S. Highly stable microtubular solid oxide fuel cells based on integrated electrolyte/anode hollow fibers. *J Power Sources.* 2015;275:362-369.
41. Zhao F, Virkar AV. Dependence of polarization in anode-supported solid oxide fuel cells on various cell parameters. *J Power Sources.* 2005;141(1):79-95.
42. Tavares MT, Alstrup I, Bernardo CA. Coking and decoking during methanation and methane decomposition on Ni-Cu supported catalysts. *Materials and Corrosion.* 1999;50(12):681-685.
43. Kim H, Lu C, Worrell WL, Vohs JM, Gorte RJ. Cu-Ni cermet anodes for direct oxidation of methane in solid-oxide fuel cells. *J Electrochem Soc.* 2002;149(3):A247-A250.
44. Xie Z, Xia C, Zhang M, Zhu W, Wang H. $\text{Ni}_{1-x}\text{Cu}_x$ alloy-based anodes for low-temperature solid oxide fuel cells with biomass-produced gas as fuel. *J Power Sources.* 2006;161(2):1056-1061.
45. Chen HW, Wang CY, Yu CH, Tseng LT, Liao PH. Carbon dioxide reforming of methane reaction catalyzed by stable nickel copper catalysts. *Catal Today.* 2004;97(2):173-180.
46. Cimenti M, Hill JM. Direct utilization of liquid fuels in SOFC for portable applications: challenges for the selection of alternative anodes. *Energies.* 2009;2(2):377-410.
47. Kagomiya I, Kaneko S, Kakimoto K, Park K, Cho KH. Fabrication and power densities of anode-supported solid oxide fuel cells with different Ni-YSZ anode functional layer thicknesses. *Fuel Cells.* 2015;15(1):90-97.
48. Hassan AA, Menzler NH, Blass G, Ali ME, Buchkremer HP, Stöver D. Development of an optimized anode functional layer for solid oxide fuel cell applications. *Adv Eng Mater.* 2002;4(3):125-129.
49. Wilson JR, Kobsiriphat W, Mendoza R, et al. Three-dimensional reconstruction of a solid-oxide fuel-cell anode. *Nature Mater.* 2006;5(7):541-544.
50. Wilson JR, Gameiro M, Mischaikow K, Kalies W, Voorhees PW, Barnett SA. Three-dimensional analysis of solid oxide fuel cell Ni-YSZ anode interconnectivity. *Microsc Microanal.* 2009;15(01):71-77.
51. Wilson JR, Barnett SA. Solid oxide fuel cell Ni-YSZ anodes: effect of composition on microstructure and performance. *Electrochem Solid St.* 2008;11(10):B181-B185.
52. Wilson JR, Cronin JS, Barnett SA. Linking the microstructure, performance and durability of Ni-yttria-stabilized zirconia solid oxide fuel cell anodes using three-dimensional focused ion beam-scanning electron microscopy imaging. *Scripta Mater.* 2011;65(2):67-72.
53. Vivet N, Chupin S, Estrade E, et al. Effect of Ni content in SOFC Ni-YSZ cermets: a three-dimensional study by FIB-SEM tomography. *J Power Sources.* 2011;196(23):9989-9997.
54. Vivet N, Chupin S, Estrade E, et al. 3D microstructural characterization of a solid oxide fuel cell anode reconstructed by focused ion beam tomography. *J Power Sources.* 2011;196(18):7541-7549.
55. Fisher JC II, Chuang SSC. Investigating the CH_4 reaction pathway on a novel LSCF anode catalyst in the SOFC. *Catal Commun.* 2009;10(6):772-776.
56. Park S, Craciun R, Vohs JM, Gorte RJ. Direct oxidation of hydrocarbons in a solid oxide fuel cell: I. Methane oxidation. *J Electrochem Soc.* 1999;146(10):3603-3605.
57. Xiao J, Xie Y, Liu J, Liu M. Deactivation of nickel-based anode in solid oxide fuel cells operated on carbon-containing fuels. *J Power Sources.* 2014;268:508-516.
58. Jiao Y, Zhang L, An W, et al. Controlled deposition and utilization of carbon on Ni-YSZ anodes of SOFCs operating on dry methane. *Energy.* 2016;113:432-443.
59. Li C, Shi Y, Cai N. Mechanism for carbon direct electrochemical reactions in a solid oxide electrolyte direct carbon fuel cell. *J Power Sources.* 2011;196(2):754-763.
60. Chen Y, Zhang Y, Lin Y, et al. Direct-methane solid oxide fuel cells with hierarchically porous Ni-based anode deposited with nanocatalyst layer. *Nano Energy.* 2014;10:1-9.

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