



## Short communication

## Simple fabrication of micro-solid oxide fuel cell supported on metal substrate

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## ABSTRACT

A simple method, without using lithography or etching processes, for fabricating a micro-solid oxide fuel cell (micro-SOFC) that utilizes a metal substrate is presented. A porous and thin (<25 μm) metal (Ni) film is fabricated by screen printing a NiO film on a ceramic substrate and subsequently reducing this film. Electrolyte and the cathode layers are sequentially deposited on the Ni-film substrate. Micro-SOFCs with a thin-film Gd-doped ceria electrolyte, supported on the Ni substrate, are successfully tested at 450 °C.

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## 1. Introduction

Micro-fuel cells are potential replacements for high efficiency and high specific energy batteries in portable power generation. To date, miniaturized fuel cells utilizing proton-exchange membranes (PEMFCs) have been the primary focus of interest. In particular, direct methanol fuel cells (DMFCs), with the benefit of direct fuel utilization, have been developed. However, concentrated methanol solution is required for DMFCs to obtain the beneficial energy output, and under operating conditions methanol cross-over is still a problem [1,2]. Due to the persistent challenges with polymer-based fuel cells, there is a growing interest in the development of micro-solid oxide fuel cells (micro-SOFCs) for portable power generation [3,4]. With these systems, hydrocarbon fuels, in addition to hydrogen, can be utilized directly at the anode and this reduces the need for the pre-reforming of fuels [5–7]. Hence, efforts are being made to develop micro-SOFCs, i.e., units based on a thin-film technique, and their fabrication can lead to new applications for SOFCs such as power supply for portable electronic devices. In order to realize micro-SOFCs, the design of the support structure for the thin-film electrolyte and the required deposition techniques have been the areas of interest.

Various approaches have been made to fabricate micro-SOFCs. Kang et al. [8] deposited a 200-nm thick yttria-stabilized zirconia (YSZ) film, using a sputtering method, on a 20-μm thick porous Ni substrate with columnar pore diameters of ~20 nm; a power density of 7 mW cm<sup>-2</sup> was obtained at 400 °C [8]. A nano-porous alumina was used as a template. The fabrication of the Ni substrate, however, was complicated in the replication process. In addition, a mass transport limitation due to the columnar pores may occur. Chen et al. [9] deposited a 2-μm thick YSZ film by a pulsed-laser deposition (PLD) method on 6-μm thick polycrystalline nickel foils, followed by photolithography and wet etching processes to yield porous nickel with a pore diameter of ~70 μm. A power output of 110 mW cm<sup>-2</sup> and an open-circuit voltage (OCV) of 0.8 V was achieved at 570 °C. Photolithography, in combination with the etching process, is complicated and often difficult since the etching process damages fuel cell materials. In addition, the resolution of wet etching is generally limited to ~10 μm. Dry etching would allow much finer patterns but is quite time-consuming for a multi-micron thick nickel substrate. Huang et al. [10] reported that micro-SOFCs developed on Si substrates, which were fabricated with the aid of sputtering, lithography, and etching processes, showed a surprisingly high power density of 400 mW cm<sup>-2</sup> at 400 °C with a YSZ electrolyte. Recently, Muecke et al. [11] found that YSZ-based micro-SOFCs prepared on glass-ceramic substrates via PLD, lithography, and etching processes delivered a power density of 150 mW cm<sup>-2</sup> at 550 °C [11]. With the above preparative techniques, it is difficult to manufacture fuel cells with a large area

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due to the inadequate mechanical strength of the free-standing electrolyte films. Unit-cell areas of  $\sim 0.06$  and  $\sim 0.04$  mm<sup>2</sup>, were obtained by Huang et al. [10] and Muecke et al. [11], respectively.

In consideration of current developments, the overall design of cell structure and the fabrication of substrate material are very important for micro-SOFCs compared with conventional SOFCs. The present study involves a simple method for fabricating micro-SOFCs utilizing a porous and thin ( $< \sim 25$   $\mu\text{m}$ ) metal (Ni) substrate. A metal substrate with a thickness of a few tens of micrometers is advantageous for micro-SOFCs since it provides good electrical conduction, high mechanical strength, and rapid start-up times due to the high thermal conduction. The porous and thin metal (Ni) substrates are obtained without using lithography or etching processes. The Ni film is fabricated by screen printing a NiO film on a ceramic substrate and subsequently reducing the printed film. The electrolyte film and the cathode are sequentially deposited on the Ni film. Nickel is a candidate for a support material since it is one of the best catalysts for hydrogen oxidation. The pore size and the thickness of the substrates are controlled by changing the particle size of NiO and by regulating the screen printing process. The latter process is a simple and clean method since it requires no special chemicals or complex apparatus. In addition, the Ni substrate can be made to have a desired pore structure that is suitable for gas diffusion and film deposition. The successful fabrication of a porous Ni structure enables fuel to reach the electrode/electrolyte interface and provides a large surface area suitable for hydrogen reduction. In this study, micro-SOFCs are constructed with a Gd-doped ceria (GDC or  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ ) thin-film electrolyte which is supported on the porous and thin Ni substrate. Ceria doped with rare-earth oxide is favourable to the intermediate-temperature operation of SOFCs due to its high ionic conductivity compared with YSZ. In addition, the small difference in the thermal expansion coefficients of GDC and Ni makes the former a better electrolyte than YSZ. The thermal expansion coefficient of YSZ (8 mol% yttria-stabilized zirconia), GDC ( $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ ) and Ni is  $10.9 \times 10^{-6} \text{ K}^{-1}$ ,  $12.4 \times 10^{-6} \text{ K}^{-1}$  and  $16.5 \times 10^{-6} \text{ K}^{-1}$ , respectively, between room temperature and  $450^\circ\text{C}$  [12–14]. In order to prevent the formation of defects such as uncovered pores on the deposited films, controlling the surface of Ni substrates is necessary. Fine ceramic powder, which tends to agglomerate due to its high specific surface area, should be well dispersed in order to obtain a printing paste of a high quality. An improved preparation method is developed in order to eliminate agglomerate formation.

## 2. Experimental procedure

NiO powder (Kojundo Chemical, Japan) was used as the starting material to fabricate the Ni substrate. The mean particle diameter of the raw NiO powder was  $\sim 1.0$   $\mu\text{m}$ , as determined with a laser particle size analyzer (CILAS 1064, France). NiO powder was mixed in an organic solution ( $\alpha$ -terpineol and ethyl cellulose in a weight ratio of 10:1) and the viscosity of the solution was controlled by adding di-ethylene glycol butyl ether. A phosphate ester-based surfactant (Rhodafac RE-610, Rhodia, Korea) and dihydroterpineol acetate were used as dispersants. The printing pastes were milled with a three-roll grinding mill (EXAKT, Germany) to break agglomerates. The further fabrication process of a micro SOFC is shown schematically in Fig. 1.

A porous Ni film was fabricated by screen printing the NiO organic solution with a 325-size mesh on a ceramic substrate and subsequently reducing the film at  $700$ – $750^\circ\text{C}$  in a hydrogen atmosphere for 3 h. The Ni film of  $\sim 22$ - $\mu\text{m}$  thickness was easily removed from the ceramic substrate after reduction and thus a free-standing, porous Ni film was obtained. The Ni film was attached to a support-

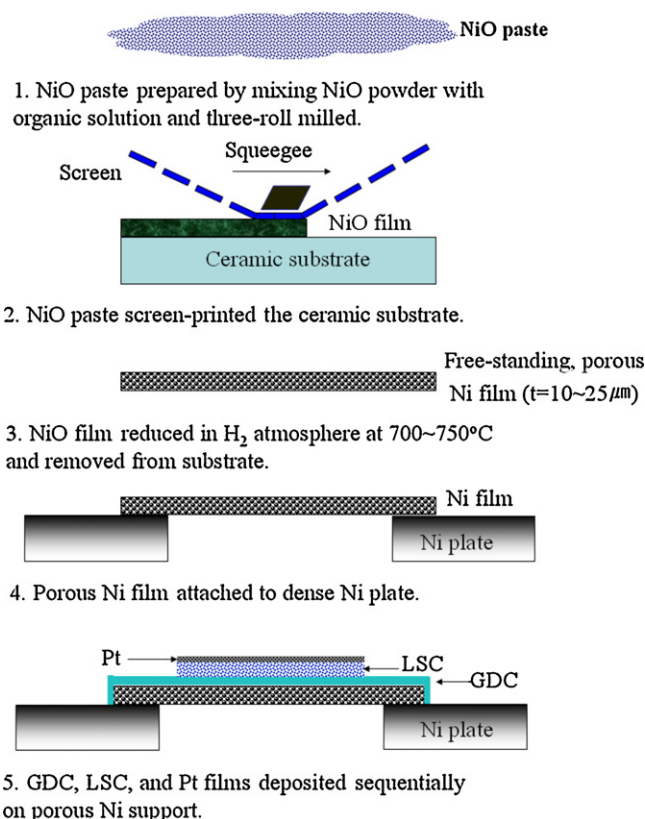


Fig. 1. Fabrication process for micro-SOFC. Note that GDC electrolyte is supported on porous nickel substrate.

ing Ni plate in a ring shape by means of Ni metal paste and then firing at  $600^\circ\text{C}$  in hydrogen atmosphere for 1 h.

A GDC thin film ( $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ , thickness  $\sim 3$   $\mu\text{m}$ ) was deposited on the Ni film by the PLD method at an oxygen partial pressure ( $\text{Po}_2$ ) of  $\sim 30$  mTorr. A stainless-steel chamber was evacuated to a base pressure of  $5 \times 10^{-6}$  Torr using a turbo molecular pump. Pulsed-laser ablation was carried out for 3 h with a KrF excimer laser (248 nm with 30 ns pulse width) at a pulse energy of  $\sim 3$  J  $\text{cm}^{-2}$  and a repetition rate of 7 Hz. The laser beam was focused on a GDC20 ( $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ ) target that rotated at  $\sim 10$  rpm. Substrates were positioned parallel to and  $\sim 5$  cm away from the target. This distance allowed sufficient interaction between the plasma plume and the background oxygen gas. The substrate temperature was maintained at  $500^\circ\text{C}$ . A porous  $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$  (LSC) cathode layer was deposited for 90 min on the GDC electrolyte at room temperature. The deposition at room temperature enabled production of LSC with a porous structure. An excimer laser with  $\sim 3$  J  $\text{cm}^{-2}$  was used with 150 mTorr ( $\text{Po}_2$ ) in the deposition chamber. In order to measure the power density of the cell, a Pt film of  $\sim 100$ -nm thickness was sputtered on top of the cathode at 3 mTorr using argon plasma from a dc sputtering chamber. Platinum paste was hand-painted on top of the sputtered Pt. The sputtered Pt film improved the adhesion between the Pt paste and the LSC cathode.

The cell was tested at  $450^\circ\text{C}$ . Fuel gas of 97%  $\text{H}_2$  + 3%  $\text{H}_2\text{O}$  was fed at a flow rate of  $20$  ml  $\text{min}^{-1}$  to the anode side and stationary air was used as the oxidant gas. Current versus cell voltage behavior was measured using an electrochemical interface (model 1287, Solartron, UK). Impedance spectra were obtained with a Gain-Phase Analyzer (Solartron SI 1260, UK). Phase analysis of the thin film was performed by means of X-ray diffraction (XRD) using  $\text{Cu K}\alpha$  radiation (MAC Science, M18XCE, Japan). The microstructure

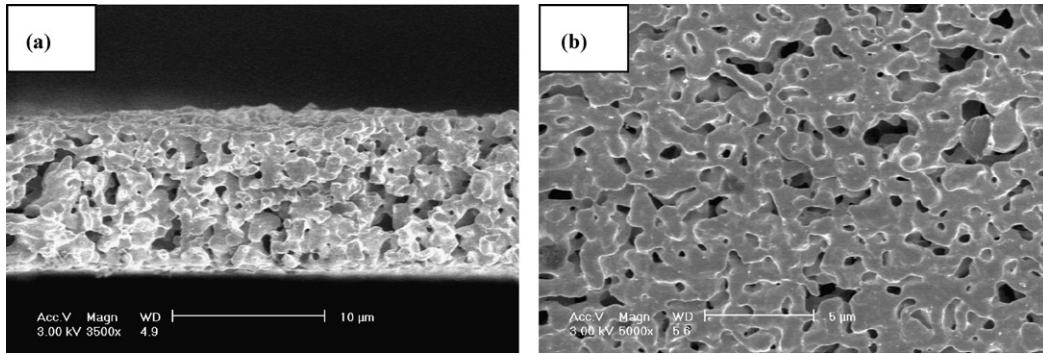


Fig. 2. (a) Cross-sectional and (b) surface SEM micrographs of free-standing Ni substrate. Thickness of Ni film may vary between 10 and 30 μm.

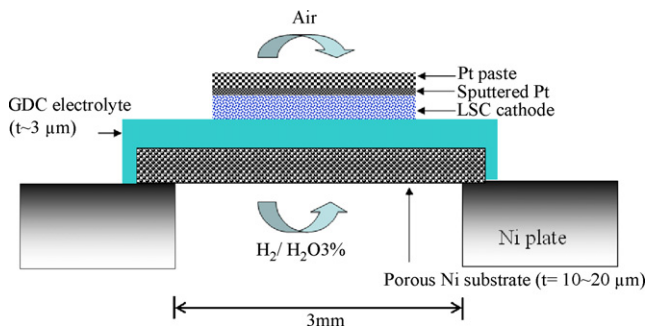


Fig. 3. Schematic of micro-SOFC (GDC thin-film supported on porous and thin Ni substrate).

was examined with a field-emission scanning-electron microscope (JEOL, model 3330F, Japan).

### 3. Results and discussion

The cross-sectional and the surface images of a Ni substrate are shown in Fig. 2. The thickness of the Ni substrate in this example is ~11 μm and the pore size is 0.2–2 μm. The porosity of the free-standing Ni film is ~30%, and is estimated from the sample weight and dimensions. The Ni substrate has a well-interconnected structure, which promises the high electrical conductivity and high mechanical strength. A schematic of the measurement cell is given in Fig. 3; the fabrication process has been described in Section 2. The use of a porous Ni substrate, strong enough to support the thin-film electrolyte of micro-SOFCs, is a key design feature. The unit-cell area of ~7 mm<sup>2</sup> employed in this study is much larger than those of other units fabricated via alternative methods [10,11].

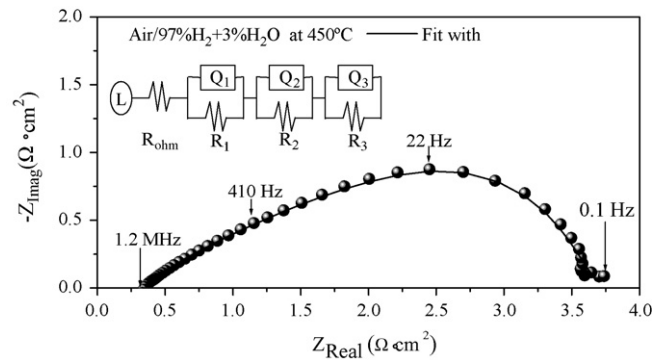


Fig. 5. Impedance spectra of micro-SOFCs measured at 450 °C. 97% H<sub>2</sub> + 3% H<sub>2</sub>O gas used as fuel gas and air as oxidant gas, representative measurement frequencies are indicated.

Cross-sectional SEM micrographs of the fabricated micro-SOFC (Ni/GDC film/LSC film) are presented in Fig. 4a ~22-μm thick Ni substrate was used. The images indicate that a ~3-μm thick GDC electrolyte covers the pores of the Ni substrate. The La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3-δ</sub> thin-film cathode, less than 1-μm thick (Fig. 4) is successfully deposited on the GDC electrolyte film. The GDC thin film shows few pores at the observed magnification. Columnar growth of the grains is apparent for the GDC film. The XRD pattern (not shown) obtained from the GDC film is consistent with reported data for a single-phase GDC with a cubic fluorite structure. No secondary phases are found within the detection limit of the XRD analysis. Electrochemical impedance spectra of the fabricated micro-SOFC measured at 450 °C are presented in Fig. 5. The spectra were obtained under open-circuit conditions with an amplitude of 0.1 V in the frequency range of 0.1 Hz to 5 MHz. The spectra were fitted using the equivalent

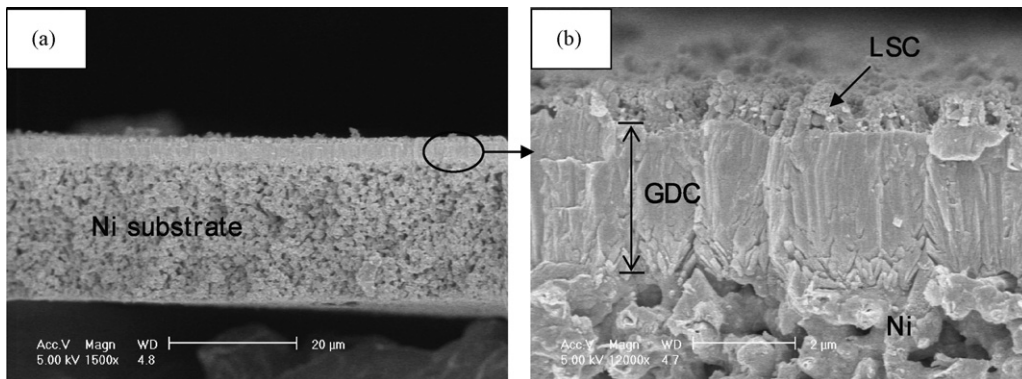


Fig. 4. Cross-sectional SEM micrographs of micro-SOFC at (a) low and (b) high magnification. GDC electrolyte ( $t \sim 3 \mu\text{m}$ ) supported on porous nickel substrate ( $t \sim 22 \mu\text{m}$ ). Thickness of LSC cathode layer is less than 1 μm.



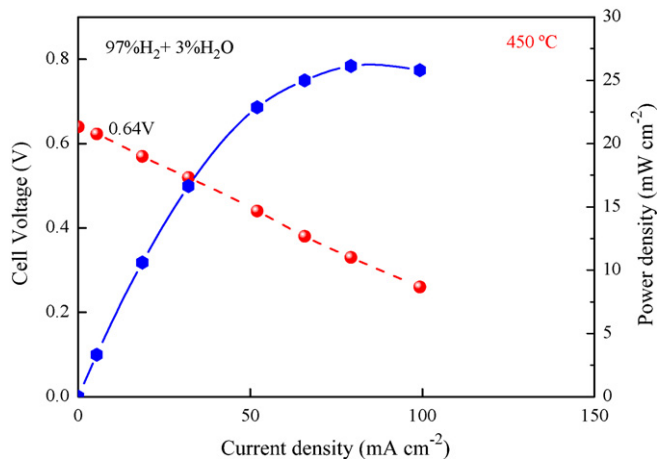


Fig. 6.  $I$  (current)– $V$  (voltage) and  $I$  (current)– $P$  (power) plots of test fuel cell at 450 °C. 97% H<sub>2</sub> + 3% H<sub>2</sub>O mixture used as fuel gas and air as oxidant gas.

lent circuit shown in Fig. 5, where  $R_{\text{ohm}}$  is the ohmic resistance,  $L$  is the inductance, and the series connection of ( $R_1$ ,  $Q_1$ ), ( $R_2$ ,  $Q_2$ ) and ( $R_3$ ,  $Q_3$ ) corresponds to the three arcs at high, middle and low frequencies, respectively.  $R_i$  is the resistance and  $Q_i$  is the constant-phase element. The three arcs correspond to three different processes contributing to the electrode reaction. The high-frequency intercept of the impedance spectra is associated with the ohmic resistance contribution of the electrolyte. The ionic conductivity of the  $\sim 3\text{-}\mu\text{m}$  thick GDC film at 450 °C is calculated to be  $\sim 8.8 \times 10^{-4} \text{ S cm}^{-1}$ . The measured ‘across-plane’ (or perpendicular to the film surface) conductivity value is slightly lower than that of a GDC film that has been reported ( $\sim 1.2 \times 10^{-3} \text{ S cm}^{-1}$ ) at 450 °C [15]. It is obvious that the area specific resistance (ASR) of the electrode is more than one order of magnitude higher than the electrolyte resistance at an open-circuit condition. This indicates that the electrode reaction process is the major determinant of cell performance. Fitting of the impedance curve shows that the  $R_1$ ,  $R_2$ , and  $R_3$  values are, respectively,  $\sim 0.81$ ,  $\sim 0.83$  and  $\sim 1.76 \Omega \text{ cm}^2$  and thus the arc at low frequencies is the largest.

Although the origin of a high ASR is not known at present, we may speculate on methods to reduce the ASR. Apparently, the composition and microstructure of Ni and LSC that were used as the anode and cathode materials, respectively, are not optimized. As a SOFC anode, Ni-electrolyte cermet is most commonly used. Nickel cermet allows the anode to spread triple-phase boundaries into a broader region of the anode film. It is not clear whether the anode is more dominating than the cathode in the ASR value. However, modification of the present anode composition is necessary for enhanced performance of the anode. With decreasing temperature, the polarization resistance of the cathode for oxygen reduction increases and thus the cathode becomes more critical than the anode in determining the performance of SOFCs. For low-temperature SOFCs, Ba-based cobaltite cathodes have given good performance due to their high mixed ionic-electronic conductivity and high oxygen surface-exchange kinetics [16]. The ASR may further be reduced if highly active electrodes such as Ba-based cobaltite and a Ni cermet, are used instead of LSC and Ni, respectively. In addition, optimization of the cathode and the anode microstructures is required.

Fig. 6 shows current ( $I$ )–voltage ( $V$ ) and current–power ( $P$ ) plots for the present Ni(anode)/GDC(electrolyte)/LSC(cathode) cell at 450 °C. The OCV value is  $\sim 0.64 \text{ V}$  and the maximum power density is  $\sim 26 \text{ mW cm}^{-2}$ . The observed OCV value is lower than the highest reported value ( $\sim 0.87 \text{ V}$  at 500 °C) for an anode-supported SOFC

that used a Sm-doped ceria (SDC) electrolyte (thickness  $\sim 10 \mu\text{m}$ ) [17]. The cause of the low OCV is not clear at present, but it may originate in part from the low activity of electrodes at low temperature [18]. An OCV of  $\sim 0.5 \text{ V}$  at 450 °C has been reported for a Pt/GDC film/Pt cell [18]. Thus, fabrication of highly active cathodes and anodes will enable increases in both OCV and power density of thin-film SOFCs. The low OCV value may also be due to structural defects in the GDC film. Although the mechanical weakness of GDC in a reducing atmosphere is well-known, reduction of GDC may no longer be a problem at 450 °C since the electrolytic domain is extended to the H<sub>2</sub>/6% H<sub>2</sub>O atmosphere as shown by Doshi et al. [19]. The low OCV value may arise partly from pin holes in the GDC film that are generated during the PLD process. Thus optimizing the film deposition process and removing structural defects may also lead to a higher OCV value.

We would like to emphasize the advantage of the present cell. The fabrication process is very simple since it does not employ complicated lithography and etching processes and thus no expensive equipment is required. The novel metal substrate provides the desired mechanical strength to support the thin-film electrolyte and a large active area is obtained. The overall thickness of the cell is  $\sim 25 \mu\text{m}$ ,  $\sim 22 \mu\text{m}$  for Ni and  $\sim 3 \mu\text{m}$  for GDC layers, which promises much higher power density per volume than with micro-SOFCs developed on Si ( $t \sim 375 \mu\text{m}$ ) [10] or glass-ceramic ( $t \sim 250 \mu\text{m}$ ) substrates [11]. The area of the present unit cell supported on porous Ni ( $\sim 7 \text{ mm}^2$ ) is more than 100 times larger than that of cells supported on Si ( $\sim 0.06 \text{ mm}^2$ ) and glass-ceramic ( $\sim 0.04 \text{ mm}^2$ ) substrates.

#### 4. Conclusions

A new design of micro-SOFC has been developed and evaluated. The micro-SOFC with a thin-film ceria electrolyte, supported on a porous and thin Ni substrate, is fabricated without using lithography and etching processes. The cell has been successfully tested at 450 °C. This investigation demonstrates that it is possible to fabricate a micro-SOFC with a large unit-cell area through the use of a metal substrate.

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