Improvement of solid oxide fuel cell by imprinted micropatterns on electrolyte

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A study is presented of an improved interfacial structure between the electrode and electrolyte of a solid oxide fuel cell. An imprint process, which is considered as a powerful tool to transcribe nano to micropatterns on materials, was employed to imprint fine patterns onto a ceramic sheet of electrolyte. In the presented work, a sheet of ceramic compound material was prepared, and micropatterns were imprinted on its surface. After debinding and sintering, a dense ceramic sheet with fine micropatterns was obtained. To investigate the effect of micropatterns on the overall performance of a fuel cell, three kinds of electrolyte sheets with different surface patterns were employed for this technique. After applying anode and cathode layers, the three fuel cell samples were assembled to test the cell performance. The result was that the finer pattern caused better performance in the three samples by exhibiting the highest overall voltage and power density, and the effective factors of patterns on ion conductivity were discussed as well. Based on the investigation, some further improved three-dimensional microstructures were proposed and fabricated by the method of micro powder imprinting (μPI).

1. Introduction: The application of solid oxide fuel cells (SOFCs) is moving towards miniaturisation and this component miniaturisation displays a huge potential in the fields of communication and information technology and biotechnology. By now, the scale of SOFCs has come to sub-micrometre, even nanometre thickness [1]. To improve the electrical capability of microSOFCs, recent researches have focused on three directions: the improvement and innovation of the material component for the electrode or electrolyte [2, 3]; the porosity of microstructure for the electrode [4]; and the reduction of electrolyte thickness and the increasing of the reactive interface between the electrolyte and electrode [5]. The improved structure of the SOFC, such as the introduction of micro/nanopatterns on to the interface could influence the final electrical properties of a fuel cell, especially when the scale of a cell comes to the micrometre or nanometre scale. Some researchers have investigated the effect of electrode–electrolyte interface shape modification on the final electrical properties of a cell by the simulation method. The numerical results showed that the cell performance was improved by applying a non-flat design to the cathode–electrolyte interface for the same amount of cathode/electrolyte materials [6, 7]. Therefore the optimisation of the reactive surface improves the diffusivity of gasses and ions. Furthermore, cell performance is affected by these factors, such as the diffusivity of gasses and ions, as well as the local ion potential, local electron potential and gas composition etc. The enhancement of performance of a fuel cell by interface modification is determined as a result of the combination effects of those factors. In this reported work, an improved interfacial structure between the electrode and electrolyte is fabricated by a new technique, and the effects of patterns on the overall performance of a cell unit are investigated.

In our previous report, we proposed an improved method of micro powder imprinting (μPI) to fabricate the ceramic thin sheets with micropatterns [8]. μPI combines the plastic imprinting process and the powder metallurgy process, such as debinding and sintering. The powder imprinting process is appropriate for small and complex-shaped components manufactured at a low cost in comparison to other traditional powder technologies, such as micropowder injection moulding and inkjet printing [9, 10]. By the μPI method, it is possible to obtain a ceramic sheet with fine microscale patterns on a single ceramic layer through fewer processes compared with the conventional method. Some kinds of micropatterns were obtained by the μPI method on the single and multilayer processed compound [11, 12]. In this Letter, the μPI method is introduced for the fabrication of the micropatterns on the surface of electrolyte sheet.

2. Micropatterned electrolyte of SOFC unit

2.1. Substrate of powder compound as electrolyte: The 8%-yttria stabilised zirconia (8YSZ) has been considered as one of the best materials of electrolyte owing to its attractive ionic conductivity, low electronic transference number and stability against the electrode materials. In this research, the feedstock powder (PXA500, TOSOH Corp.) for the powder injection moulding process was employed as the processed powder compound, in which the nanometre scale (average size of particle is about 600 nm) YSZ powders were kneaded with organic binders.

2.2. Transcription of micropatterns by μPI method: The YSZ compound, which was pre-pressed into a sheet, was placed in the pressing container as shown in the schematic apparatus of the thermal imprinting system depicted in Fig. 1*a*. The thickness of the printed ceramic sheet can be controlled by the finishing position of the punch, which was adjusted by the imprinting press. Thermal imprinting was carried out at 140°C. The heating ratio, holding time and cooling ratio were 30°C min^{-1}, 5 min and 10°C min^{-1}, respectively. Meanwhile, the imprinting was operated in vacuum to prevent bubbles in the processed sheet of the YSZ compound. As a result of imprinting, the micropatterns were transcribed onto the surface of a ceramic compound sheet.

Elastic polymer sheets of polydimethylsiloxane (PDMS), on which the micropatterns were transcribed, were employed as moulds for thermal imprinting. The fabricating process of the mould involved casting, bubble removing in vacuum and curing by heating. The cured PDMS was flexible, and was able to prevent the compound sheet from breaking while the mould was removed from the thin ceramic sheet. One type of micropatterns, arrays of circular-cone shaped pillars, is shown as an example in Fig. 1*b*.

The ceramic sheets of YSZ with an imprinted pattern were debound and sintered in the air atmosphere. A continuous debinding and sintering procedure was adopted in this work. The debinding temperatures were among 200–500°C, in which the heating rate was 30°C h^{-1}. The sintering temperature was set at 1500°C and the holding time was 2 h. As a result, solidified and dense micropatterns were obtained on the thin sheet of ceramic. Fig. 2 shows arrays of

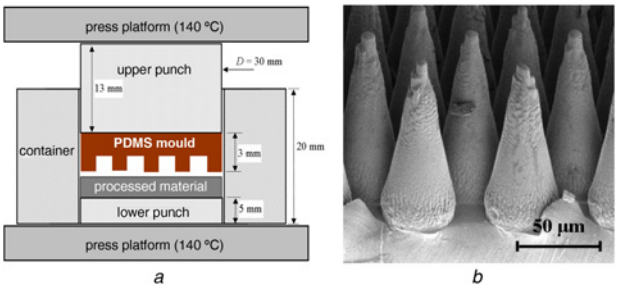

Figure 1 *Imprinting system and mould*
a Schematic apparatus of thermal imprinting system in which YSZ compound was employed as the processed material in this study
b SEM images of arrays of circular-cone shaped pillars on the surface of PDMS mould, which were obtained by casting method

microcircular-cone shaped holes on the sintered sheet of YSZ ceramic as an example and the sintered shape was in accord with the shape of the PDMS mould in Fig. 1*b*.

2.3. Assembling of SOFC testing unit: Both cathode paste (YSZ + LSM + binders) and anode ceramics paste (YSZ + NiO + binders) were screen printed on the surface of the sintered electrolyte sheet, respectively, and sintered at 1150°C subsequently [13]. To investigate the effect of patterns of the electrolyte only, for each testing SOFC unit, the thicknesses of sintered electrodes were both fixed to 60 μm by fixing the thickness of the mask during screen print. The size of both the anode and the cathode square region were fixed to 8 × 8 mm.

2.4. Testing of SOFC unit: The automatic SOFC testing systems (Auto-SOFC, TOYO Corporation) were employed to evaluate the electrical capability of the cell units. The system contains two parts: working part (furnace, gas supporting system and fuel cell) and evaluating part (software and computer). The schematic drawing of the evaluating system is depicted in Fig. 3.

For electrochemical characterisations, the cell was heated at a rate of 200°C h^{-1} up to 800°C. Subsequently, 3%-humidified hydrogen gas for reduction of NiO to Ni metal and fuel was supplied to the anode side, and dry air as oxidant with a flow rate of 150 ml min^{-1} was supplied to the cathode for 1 h, respectively. Dual alumina inner tubes were used for supplying reactant gases which were subsequently exhausted through the space between the inner tube and the outer tube. The fuel flow tubes were kept at 120°C to ensure that no condensation of water would take place between the humidifier and the furnace. Once the SOFC reached its operational temperature, the open circuit voltage and the current were monitored automatically.

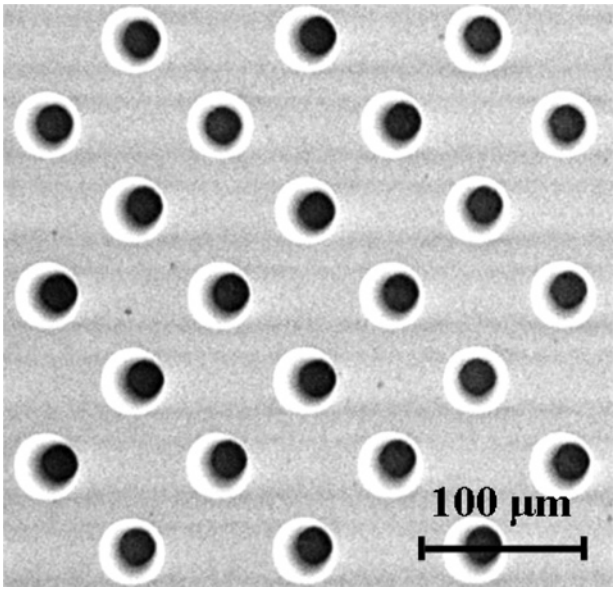

Figure 2 *SEM image of sintered arrays of circular-cone shaped holes on sheet of YSZ ceramic, which show the according shapes with the mould of the PDMS*

3. Results and discussion

3.1. Effect of micropatterns of electrolyte on the overall performance of a cell: Terminal voltage and power density are two of the important characteristics for evaluating the electrical performance of a SOFC. To investigate the effect of the patterns on the final performance of the SOFC unit, three types of testing units were prepared in this work. Sample-A had nearly flat surfaces of electrolyte and the thickness was about 500 μm. Sample-B had millimetre scale square patterns with depth of 600 μm, and the minimum thickness of the electrolyte was about 500 μm by controlling the thickness of the imprinted ceramic sheet. It is noted that the patterns were transplanted 'on' the electrolyte of 500 μm. The increased total interface area for sample-B from sample-A was about 70%. Sample-C had the arrays of circular-cone microholes 'in' the 500 μm-thick electrolyte sheet. The depth of the circular-cone holes was about 100 μm when the diameter of the bottom circle of the circular cone was 40 μm. The total interface area for sample-C was increased by about 30% from sample-A. The dimensions and morphologies of these SOFC units are shown in Fig. 4.

Fig. 5 shows an experimental example for samples A, B and C, where the cell performance is enhanced by cathode–electrolyte interface modification. Figs. 5*a* and *b* compare the current–voltage curves and current–power curves which were obtained from three cells with different morphology of electrolyte at 800°C. It is found that decreasing the value of voltage causes the current density to decrease (Fig. 5*a*), whilst increasing the power density causes the current density to increase (Fig. 5*b*).

There are some other important conclusions from the evaluated results. The first is that the voltage and the power density in sample-B were higher than those in sample-A, which had the same minimum thickness of electrolyte. The current density obtained from sample-B (with microsquare patterns) is always larger than that from sample-A (with the flat electrolyte) when it is compared at the same terminal voltage. This result shows that

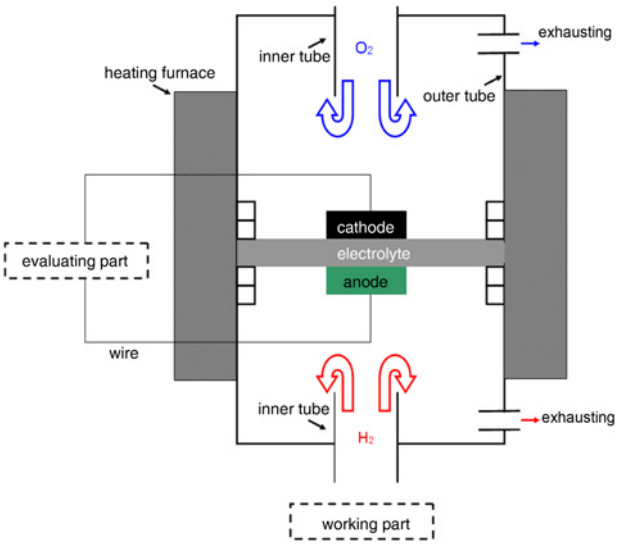

Figure 3 *Schematic graph of auto evaluation system for SOFC unit which contains two parts: working part and evaluating part*

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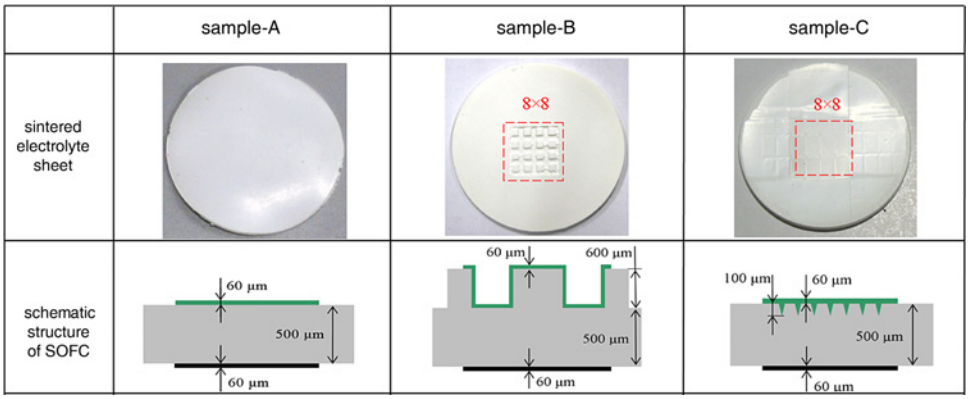

Figure 4 *SEM images of sintered arrays of circular-cone shaped holes on sheet of YSZ ceramic*
Sample-A has nearly flat surfaces of electrolyte and thickness is 500 μm
Sample-B has millimetre scale square patterns with depth of 600 μm, minimum thickness of electrolyte is about 500 μm
Sample-C has arrays of circular-cone microholes in 500 μm-thick electrolyte sheet
Depth of circular-cone holes is about 100 μm

the patterned interface caused better performance than the flat one; even the volume of electrolyte material was increased. The reason could be that the patterns increase the reactive area of the interface of the electrolyte/cathode and the mass of ion transmission is increased as a result. The second important conclusion from Fig. 5 is that both the values of terminal voltage and power density obtained from sample-C (with microholes in the electrolyte) were larger than those from sample-A and sample-B when they are compared at the same current density. Even the total enlargement for the interface area of sample-C is less that that of sample-B. The reason could be that the patterns of the holes in the electrolyte of sample-C not only increased the reactive area but also decreased resistance by reducing the thickness of the electrolyte. As a result, loss of resistance for a cell would be decreased. Therefore sample-C showed the best performance among all samples.

3.2. Improved structure for SOFC: Based on the investigation for the overall performance of SOFC units in which different patterns were employed on the interface of the electrolyte/electrode, it was found that the micropatterns bring improvement for the SOFC. The cell performance is affected by many factors, such as local ion potential, local electron potential and gas composition etc. The enhancement of the performance of the fuel cell by interface modification is determined as a result of the combination effects of those factors. The appropriate employment of patterns not only increases the reactive area but also decreases the minimum thickness of electrolyte. Consequently, the inner loss of resistance of a cell is decreased as well. Furthermore, such a structure also influences the detailed distributions of electric potentials, gas

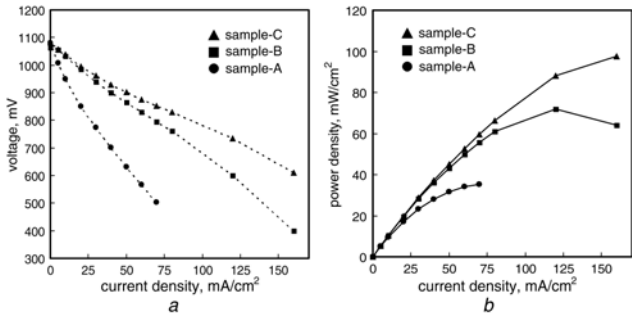

Figure 5 *Evaluated parameters for performances of samples A, B and C at 800°C*
a Values of terminal voltage
b Power density

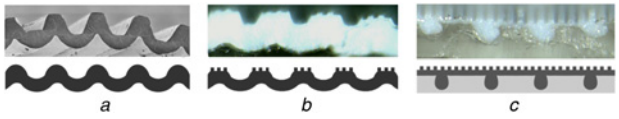

Figure 6 *SEM images and schematic graphs of some 3D microstructures of electrolyte by μPI method*
a Microcorrugated sheet by imprinting and sintering on bilayer substrate of ceramic-polymer
b Microcorrugated sheet with additive patterns by multistep imprinting and sintering on bilayer substrates
c Both-surfaces-patterned sheet by multistep imprinting on bilayer substrates

concentrations and the local electrochemical reaction rate, which has been investigated by numerical simulation [6]. Therefore the micropatterned structure has potential utilisation for improvement of SOFC performance, especially for the electrolyte-supporting cells and microscale cells.

Besides the micropatterns which are reported above, some other improved micro three-dimensional (3D) structures for electrolyte have been fabricated by the method of μPI. These 3D structures include the corrugating sheet in Fig. 6*a* by imprinting on a bilayer substrate of ceramic-polymer, the microcorrugated sheet with additive patterns by multistep imprinting on a bilayer substrates in Fig. 6*b*, and the both-surfaces-patterned sheet by multistep imprinting on bilayer substrates in Fig. 6*c*. The contribution of these micro3D structures on overall performance will be investigated in future work.

4. Conclusions: In this Letter, the micropatterns were transcribed onto the interface between the electrolyte and anode of the SOFC unit by the μPI method. According to the test results of terminal voltage and power density with a nearly flat interface and patterned interface, the patterns increased the reactive area and the patterned electrolyte showed better performance than the flat one as a result. Another conclusion was that the performance of the sample with hole-patterns in the electrolyte was better than for other samples. Therefore designing the structure for a SOFC, the approach of increasing reactive area by introducing the patterns on the sheet of electrolyte should be considered first. Secondly, the patterns (such as the holes in the electrolyte) should be helpful to reduce the thickness or inner loss of the SOFC. There are many possible structures between electrolyte and electrodes, so that our future work is to optimise this interface.

In this Letter, the micropowder imprinting method on a single side of the electrolyte layer has been introduced. We showed patterns on both surfaces of the electrolyte by the improved μPI

process in the final Section. In coming work, we will show the effect of the patterns on both sides of the electrolyte.

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