

# FABRICATION OF PROTON-CONDUCTIVE BZY-BASED LOW-TEMPERATURE MICRO SOLID OXIDE FUEL CELL

Tomokazu Takahashi<sup>1\*</sup>, Fumitada Iguchi<sup>2</sup>, Hiroo Yugami<sup>2</sup>, Masayoshi Esashi<sup>3</sup>, and Shuji Tanaka<sup>1</sup>

<sup>1</sup>Nanomechanics, Tohoku University, Sendai

<sup>2</sup>Mechanical Systems and Design, Tohoku University, Sendai

<sup>3</sup>World Premier International Research Center Advanced Institute for Materials Research, Tohoku University, Sendai

**Abstract:** This paper describes the fabrication of the micro SOFC using a proton-conductive yttrium-doped barium zirconate (BZY) membrane. The proton-conductive electrolyte makes a fuel supply system simpler in comparison with conventional oxygen-conductive electrolyte like yttria stabilized zirconia (YSZ). In addition, BZY is expected to work at low temperature (~600 °C). A 200 nm thick BZY film was deposited by pulse laser deposition (PLD), and the film stress was reduced by controlling partial oxygen pressure during deposition. A microheater is buried in the membrane for local heating in startup. The function of the microheater was confirmed by thermograph.

**Keywords:** micro solid oxide fuel cell (micro SOFC), proton conductive solid oxide electrolyte, yttrium-doped barium zirconate (BZY)

## INTRODUCTION

Recently, increasing demand for the longer operation time of portable devices makes fuel cells attractive for portable energy sources. Several types of fuel cell have been widely studied, e.g. direct methanol fuel cell (DMFC), polymer electrolyte membrane fuel cell (PEFC) with fuel reformer, PEFC with hydrogen storage and solid oxide fuel cell (SOFC).

At present, the power density of micro DMFC and PEFC is still low. Therefore, a large cell is needed to supply power required by applications, and a volume available for a fuel cartridge becomes small in the limited volume of portable devices. Consequently, the operation time by a single refueling is limited, and in addition, the large cell will raise the cost of fuel cell systems. SOFC has a higher power density in comparison with DMFC [1], and has potential to replace DMFC and PEFC for portable uses, if problems deriving from its high operation temperature (e.g. 800–1000 °C) are solved. In addition, monolithic micro SOFC can be fabricated on a Si wafer by a wafer-level batch process including thin film deposition and etching.

To date, several micro SOFC were reported [2-6], but all of them used oxygen-conductive solid oxide electrolytes such as Y stabilized ZrO<sub>2</sub> (YSZ) [4] and Gd-doped CeO<sub>2</sub> (GDC) [5]. Considering system configuration, a proton-conductive fuel cell is simpler and thus suitable for miniaturization, because generated water does not mix with fuel and just simply discharges from the cathode. In this study, the

proton-conductive solid oxide electrolyte is used. The electrolyte membrane is made of Y-doped BaZrO<sub>3</sub> (BZY), which has high proton conductivity at low temperature (~600 °C). Further reduction of operation temperature is possible by making the BZY membrane extremely thin.

## STRUCTURE

Figure 1 shows the structure of a micro SOFC. The electrolyte membrane is made of BZY. In this study, the BZY membrane is ca. 200 nm thick, and is self-supported for thermal isolation. Corrugation is formed to relax the intrinsic and thermal stress of the membrane. A Ta/Pt/Ta microheater is embedded in a SiO<sub>2</sub> insulation layer, which is surrounding and supporting the BZY membrane. The microheater is necessary to start up the fuel cell by locally heating the membrane. The anode and cathode electrodes are sputter-deposited porous Pt-Pd.

## EXPERIMENTAL

### Fabrication

Figure 2 shows the fabrication process of the micro SOFC. First, a Si substrate is wet-etched using a SiO<sub>2</sub> mask to form corrugated patterns (b–d). Low-stress SiO<sub>2</sub> is deposited by TEOS (tetraethyl orthosilicate) plasma CVD, and on the topside, the Ta/Pt/Ta microheaters and Ta/Pt/Au/Pt/Ta wirings are formed. Low-stress SiO<sub>2</sub> is again deposited on the topside for electrical insulation (e), and then patterned to open BZY membrane windows (f). BZY is deposited by pulsed laser deposition (PLD) with a

stencil mask (g). Forth harmonic generation (FHG) Nd:YAG laser with a pulse width of 150 ns and a pulse energy of 40 mJ is used to abrade a sintered BZY ceramic pellet. The thickness of BZY is 200 nm.

The BZY membrane is released by etching Si from the bottom side by TMAM followed by XeF<sub>2</sub>. A SiO<sub>2</sub> mask is formed on the backside (h), and the topside is protected by an alkaline-protective polymer (ProTEK B3, Brewer Science, Inc.) (i). After TMAH etching, the backside SiO<sub>2</sub> mask as well as the ProTEK B3 coating are removed (k), because the SiO<sub>2</sub> mask forms "eaves" at the edges of the etched window, which cause the disconnection of Pt/Ti metal wiring deposited with a stencil mask (m). Finally, the porous Pt-Pd is deposited as catalytic electrodes on both sides by dc sputtering method with stencil masks (n). The fabricated micro SOFC is shown in Figure 3.

### Stress control of solid oxide electrolyte

The stress control of the BZY film is important for making a very thin self-supported BZY membrane. The residual stress of the BZY film is caused by chemical strain as well as the difference of coefficients of thermal expansion (CTE) between BZY and Si.

The chemical strain is dependent on the concentration of oxygen defects in solid oxide electrolyte. It was reported that the oxygen defects electrically repel each other and expand the grid interval of GDC, resulting in compressive stress [7]. Because the oxygen defects decrease with increase in partial O<sub>2</sub> pressure during deposition, the chemical strain is expected to reduce at high partial oxygen pressure. Figure 4 shows the relationship between partial O<sub>2</sub> pressure and the residual stress of a GDC membrane [5]. A similar relationship was observed for a 200 nm thick BZY membranes deposited at 900 °C. The residual stress of the BZY membrane is nearly zero at a partial oxygen pressure of 0.1 Torr.

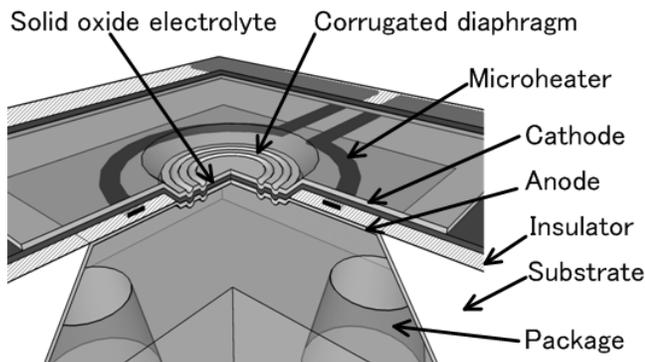


Fig. 1: Schematic of the micro SOFC with a microheater

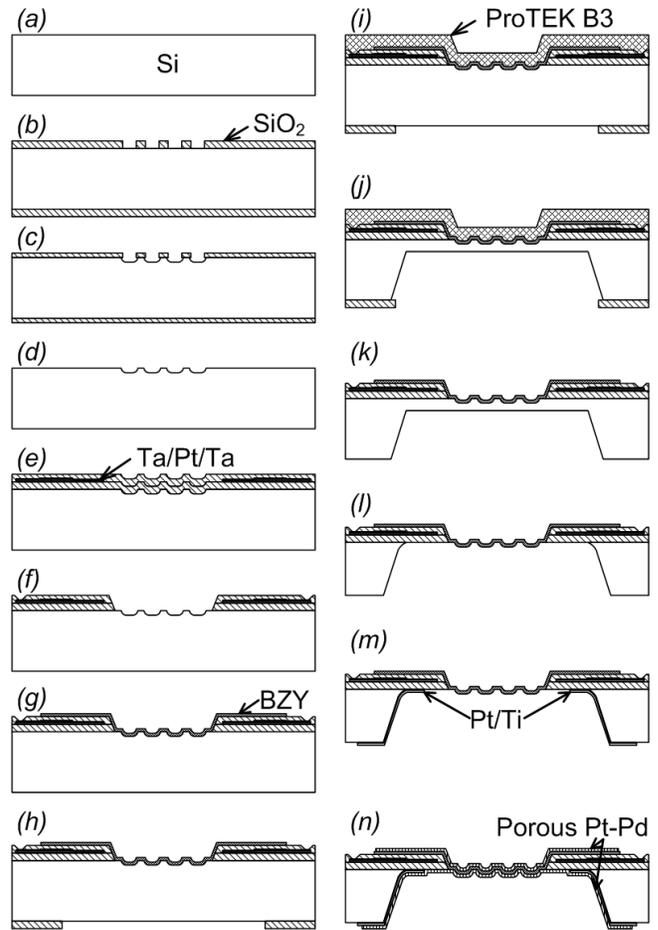


Fig.2: Fabrication process of the micro SOFC with a microheater

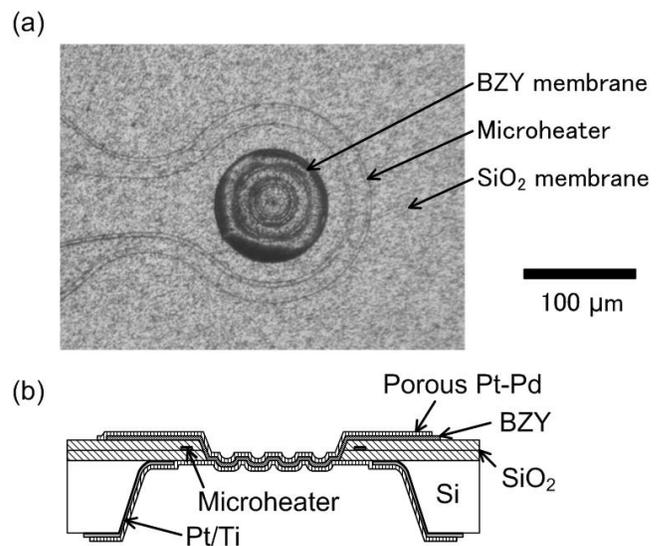


Fig.3: Micro SOFC with a microheater

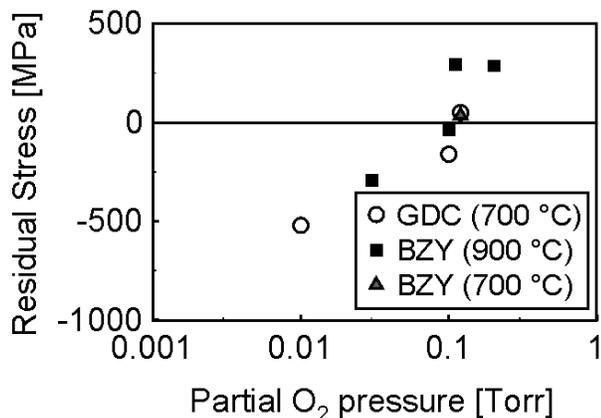


Fig.4: Stress control of solid oxide electrolyte by partial O<sub>2</sub> pressure

### Evaluation setup

For evaluation, electrical and fluidic connections were made to the micro SOFC, as shown in Figure 5. Two kinds of metal wire, i.e. one for supplying power to the microheater and the other for measuring fuel cell output, are connected to Ta/Pt/Au pads with conductive epoxy. For feeding the micro SOFC with hydrogen, a glass substrate with sandblasted channels and through holes is bonded to the backside of the micro SOFC with epoxy adhesive. On it, a glass tube is fixed with the same epoxy adhesive. Figure 6 shows the micro SOFC ready for evaluation.

Figure 7 illustrates a measurement setup for the micro SOFC. Hydrogen is fed to the micro SOFC through a mass flow controller (MFC) and a water bubbling bottle. Wet hydrogen is used to prevent the BZY membrane from being reduced. The surface of the micro SOFC is observed by an infrared camera. Figure 8 shows the thermograph of the micro SOFC in which the microheater was heated at 250 °C and hydrogen was flowing at 8 sccm. The temperature of the microheater was determined based on the relationship between the temperature and resistance of the microheater, which was measured in advance. The thermograph confirmed that the heating area was localized on the membrane. At this time, 16.4 mW (11.6 mA, 1.41 V) was consumed by the microheater.

The membrane was heated up to 500 °C, but no significant output was observed from the micro SOFC. Impedance measurement suggested that electrolyte resistance was sufficiently low ( $\sim 0.1 \Omega\text{cm}^2$  in area specific resistance), but reaction resistance at the catalytic electrodes was extremely high ( $>100 \Omega\text{cm}^2$ ) probably due to the morphology change of porous Pt-Pd at high temperature.

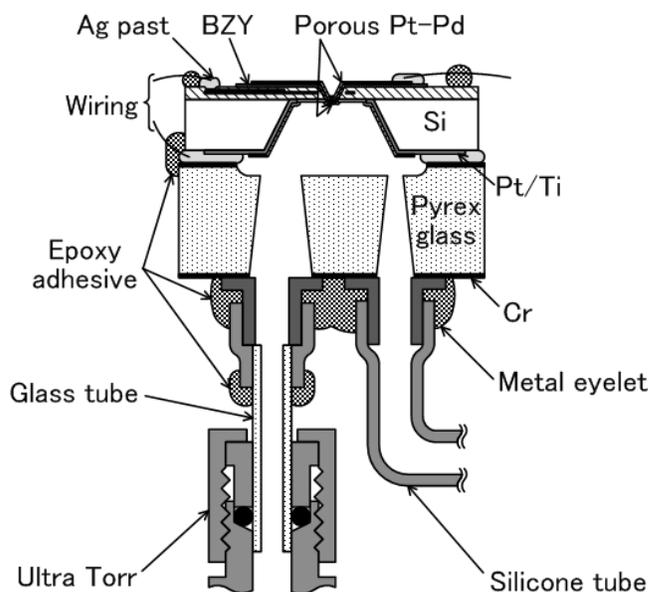


Fig.5: Schematic of the cross-section of the packaged micro SOFC with a microheater

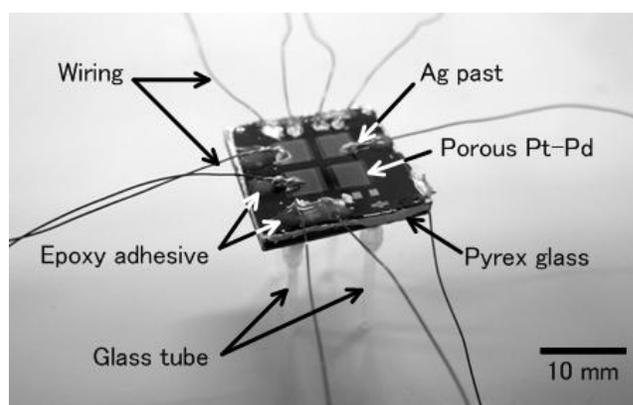


Fig.6: Photograph of the packaged micro SOFC with a microheater

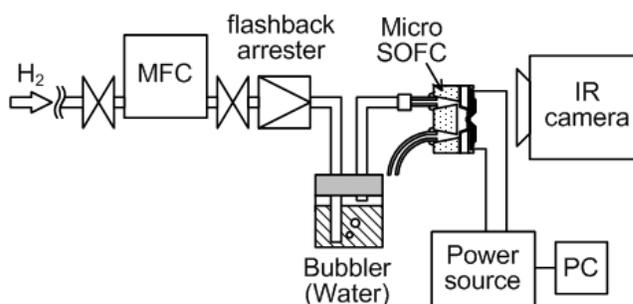


Fig.7: Measurement setup for the micro SOFC

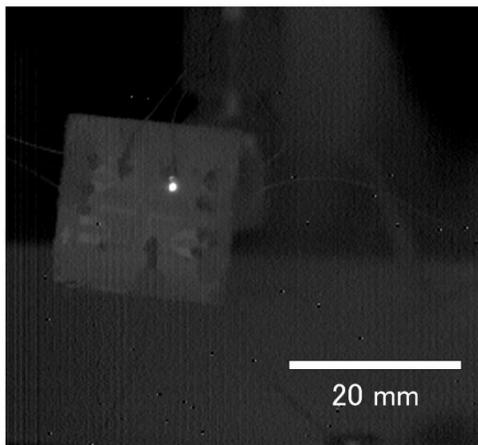


Fig.8: Thermograph of the top of the micro SOFC

## CONCLUSION

This paper described the fabrication of the micro SOFC using a ca. 200 nm thick proton-conductive BZY membrane. The proton-conductive electrolyte makes a fuel supply system simpler in comparison with conventional oxygen-conductive electrolyte like YSZ. In addition, BZY is expected to work at low temperature (~600 °C), and further temperature reduction is possible by making the membrane thinner.

The structure of the micro SOFC was successfully fabricated. A BZY film was deposited by PLD, and the stress of the BZY film was made slightly tensile (40 MPa) by controlling partial O<sub>2</sub> pressure during deposition. A microheater is buried in the membrane for local heating in startup. After piping and wiring, the microheater was heated at 250 °C under observation by an infrared camera. The thermograph confirmed that the heating area was localized on the membrane. At this time, 16.4 mW (11.6 mA, 1.41 V) was consumed by the microheater.

## ACKNOWLEDGEMENTS

This study was performed in R&D Center of Excellence for Integrated Microsystems, Tohoku University under the program “Formation of Innovation Center for Fusion of Advanced Technologies” supported by Special Coordination Funds for Promoting Science and Technology, and as a part of Creative Scientific Research Program No. 18GS0203 “Nano-energy System Creation” supported by the Ministry of Education, Science, Culture and Sports.

## REFERENCES

- [1] Sakaue E 2005 Micromachining / Nanotechnology in Direct Methanol Fuel cell *Proc. IEEE MEMS 2005* (Florida, Jan. 30 – Feb. 3, 2005) 600 – 605
- [2] Huang H, Nakamura M, Su P, Fasching R, Saito Y and Prinz F B 2007 High-performance Ultrathin Solid Oxide Fuel Cells for Low-temperature Operation *J. Electrochem. Soc.* **154** B20 – B24
- [3] Hütter A B, Beckel D, Infortuna A, Muecke U P, Rupp J L M, Gauckler L J, Mermet S R, Muralt P, Bieri N R, Hotz N, Stutz M J, Poulikakos D, Heeb P, Müller P, Bernard A, Gmür R and Hocker T 2008 A micro-solid Oxide Fuel Cell System as Battery Replacement *J. Power Sources* **177** 123 – 130
- [4] Su P C, Chao C C, Shim J H, Fasching R and Prinz F B 2008 Solid Oxide Fuel Cell with Corrugated Thin Film Electrolyte *Nano Lett.* **8** 2289 – 2292
- [5] Takahashi T, Iguchi F, Yugami H, Esashi M and Tanaka S 2009 Deposition and Microfabrication of Gd-doped CeO<sub>2</sub> for Micro SOFC Operating at Low temperature *Transactions of Japan Society of Mechanical Engineers* **75** 138 – 140
- [6] Anna E, Anja B H, Jennifer L M R and Ludwig J G 2009 Review on microfabricated micro-solid oxide fuel cell membranes *Journal of Power Sources* **194** 119-129
- [7] Lubomirsky, I 2006 Mechanical properties and defect chemistry *Solid State Ionics* **177** 1639 – 1642