A Silicon-Based Nanothin Film Solid Oxide Fuel Cell Array with Edge Reinforced Support for Enhanced Thermal Mechanical Stability

Baek, Jong Dae; Yu, Chen-Chiang; Su, Pei-Chen

2016

Baek, J. D., Yu, C.-C., & Su, P.-C. (2016). A Silicon-Based Nanothin Film Solid Oxide Fuel Cell Array with Edge Reinforced Support for Enhanced Thermal Mechanical Stability. *Nano Letters*, 16(4), 2413-2417.

<https://hdl.handle.net/10356/85446>

<https://doi.org/10.1021/acs.nanolett.5b05221>

© 2016 American Chemical Society. This is the author created version of a work that has been peer reviewed and accepted for publication by *Nano Letters*, American Chemical Society. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1021/acs.nanolett.5b05221>].

Downloaded on 26 Apr 2023 23:17:11 SGT

A Silicon-based Nano-Thin Film Solid Oxide Fuel
Cell Array with Enhanced Thermal Mechanical
Stability

Jong Dae Baek[†], Chen-Chiang Yu^{†, ‡}, Pei-Chen Su^{†,}*

[†]School of Mechanical and Aerospace Engineering, Nanyang Technological University,
Singapore

[‡]Energy Research Institute, Interdisciplinary Graduate School, Nanyang Technological
University, Singapore

KEYWORDS: Micro-solid oxide fuel cell, Nano-thin film electrolyte array, Silicon
micromachining process, Thermal mechanical stability, Thermal cycling.

ABSTRACT

A silicon-based micro-solid oxide fuel cell (μ -SOFC) with electrolyte membrane array embedded in a thin silicon supporting membrane, featuring a unique edge reinforcement structure, was demonstrated by utilizing simple silicon micromachining processes. The square silicon supporting membrane, fabricated by combining deep reactive ion etching and through-wafer wet etching processes, has thicker edges and corners than the center portion of the membrane, which effectively improved the mechanical stability of the entire fuel cell array during cell fabrication and cell operation. The 20 μ m-thick, single crystalline silicon membrane supports a large number of 80 nm-thick free-standing yttria-stabilized zirconia (YSZ) electrolytes. The fuel cell array was stably maintained at the open circuit voltage (OCV) of 1.04 V for more than 30 hours of operation at 350 °C. A high peak power density of 317 mW/cm² was obtained at 400 °C. During a rigorous *in-situ* thermal cycling between 150 and 400 °C at a fast cooling and heating rate of 25 °C/min, the OCV of the micro-SOFC recovered to its high value of 1.07 V without any drop caused by membrane failure, which justifies the superior thermal stability of this novel cell architecture.

TEXT

Micro-solid oxide fuel cells (μ -SOFCs) featuring nano-thin film electrolytes have attracted great attention for ultra-low temperature SOFCs operating below 500 °C. By reducing the electrolyte thickness from tens of micrometers to tens of nanometers, the high ohmic resistance from the thermally-driven ionic charge transfer process has been drastically minimized for a high cell performance at such low operating temperatures.¹ The realization of such nanoscale thin electrolyte SOFCs was first demonstrated by using silicon micromachining process together with the thin film deposition technologies such as sputtering,²⁻⁶ atomic layer deposition (ALD),⁷⁻¹⁰ or pulsed-laser deposition (PLD)¹¹⁻¹⁶ for the nano-thin film electrolyte fabrication. A number of successful demonstrations of μ -SOFCs have been reported with impressively high cell performances below 500 °C for the past decade.^{2-5, 7-11, 17}

Due to the extremely small thickness of the free-standing oxide electrolyte, the mechanical strength and stability of the fragile electrolyte membrane are one of the key considerations for successful operations of silicon-based μ -SOFCs. To ensure the membrane mechanical stability, the lateral dimension of the membrane is usually kept small since the membrane residual stress is directly proportional to its lateral dimension.¹⁸ A 100 nm-thick, free-standing yttria-stabilized zirconia (YSZ) membrane is typically confined within a lateral dimension of only few hundred micrometers or less, but this has limited the available electrochemically active area of the fuel cell.^{2-4, 9, 10, 19} Although superior power densities at reduced temperatures have been reported, the tininess of such μ -SOFC nano-thin film membranes gives trivial power outputs of only micro-watts, thereby limiting their applications as practical power sources.

For silicon-based μ -SOFCs to move forward into commercially feasible stage, it is necessary to utilize the ease of silicon micromachining techniques to create a suitable structure that can

1
2
3 accommodate the inherent residual stresses of the membrane components, namely the deposited
4 thin film cathode, electrolyte, and anode assembly. In addition, the lateral dimension of the
5 effective membrane area needs to increase to obtain higher total power output from a single chip
6 to deliver practically usable rate power. For such purpose, various techniques have been
7 attempted. Tsuchiya *et al.* demonstrated 5 mm $\times$ 5 mm square YSZ electrolyte with thickness of
8 54 nm supported by relatively thick metallic grids as shown in figure 1(a) and impressive total
9 power output ($\sim$ 21 mW at 510 $^{\circ}$ C) was reported.⁶ However, nanoscale thin square membrane
10 introduced severe buckling and wrinkles which can deteriorate membrane mechanical stability,¹⁷
11 and thick metallic grids located directly on large-scale free-standing membrane can make
12 membrane stress more complex and additional stress can be imposed on the membrane.
13 Moreover, the regions covered by supporting grids hinder effective catalytic reactions, which can
14 limit cell performances and fabrication process is also much complicated.

15
16
17 As another approach, Su *et al.* first reported a silicon-based μ -SOFC with a corrugated nano-
18 thin film electrolyte (figure 1(b-c)).^{8, 20} The free-standing YSZ electrolyte membrane was
19 fabricated using a single crystalline silicon as a template to generate corrugations within the
20 membrane, which is mechanically more compliant to effectively alleviate the membrane residual
21 stress.²¹ The lateral dimension of YSZ membrane was able to scale up to 600 μ m and additional
22 reaction surface area introduced by membrane corrugation also provided extra current output.
23 However, the free-standing electrolyte membrane with thickness of only 70 nm was still too
24 fragile with such a large lateral dimension to be in practical fuel cell configuration. This is
25 mainly due to the weak heterogeneous junctions between the free-standing corrugated electrolyte
26 membrane and the supporting silicon substrate (as pointed by red arrow in figure 1(b)), which are
27 geometrical and material discontinuities that resulted in high stress concentration points. The
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

unstable stress behavior at the vicinity of the hetero-junctions was also verified by numerical modelling using the energy method of classical stability analysis.¹⁸ Therefore, instead of attempting to further enlarge the lateral dimension of the nano-thin film electrolyte membrane, Su *et al.* later introduced another fabrication method to increase the surface utilization density of membranes by integrating a sheer number of electrolyte membranes into a sturdier supporting membrane, where the nano-thin membranes still remained a small lateral dimension of only 50 μm for reliable mechanical stability (figure 1(c)).²⁰ Unlike the previous work where the large and very thin electrolyte membrane was left completely free-standing without an intermediate support, the small electrolyte membrane arrays were integrated onto a 3-5 μm -thick, stress-free, and single-crystal silicon membrane support. The electrolyte membranes were circular in shape and arranged in close-packed fashion with a small separation to maximize the surface utilization rate within a limited area. A membrane electrolyte array with lateral dimension of up to 6 mm $\times$ 6 mm was demonstrated and can be further scaled up easily with same method, and a high surface utilization rate of 90% can be realized with the technique reported.

The main issue of the structure reported by Su *et al.* is the faster etching rate at the junction between (100) and (111) planes during silicon wet etching with alkaline solution,²² as pointed by red arrows in figure 1(c). The resulted silicon supporting membrane is much thinner at the four corners and the four edges, which created another stress-concentration site that caused additional failure occurrence both during the cell fabrication process and the cell operation.

Figure 1. Cross-sectional schematics for silicon-based μ -SOFCs to increase total power output reported previously.^{6, 8, 20} (a) YSZ electrolyte supported by a thick Pt grid. (b) Free-standing corrugated YSZ electrolyte. (c) Silicon membrane-supported YSZ electrolyte (The red arrows indicate the mechanically weak hetero-junctions between the corrugate electrolyte and the silicon substrate).

In this regard, we here demonstrated a simple fabrication method to further reinforce the mechanical strength of the thin silicon membrane in the μ -SOFC array developed previously.²⁰

The square silicon supporting membrane for the YSZ membrane array was reinforced by leaving thicker silicon at the four edges and four corners. The thicker support was created by combination of deep reactive ion etching (DRIE) and anisotropic chemical wet etching with alkaline solution to compensate for the over-etching occurred at the corners between (100)/(111) silicon surfaces. A rigorous thermal cycling test was performed to verify the thermal mechanical stability of the fuel cell array.

The main focus of the structure fabrication is to create a silicon diaphragm that is thicker at the edges to compensate for the corner over-etching typically observed when fabricating a silicon diaphragm using (100) single crystalline silicon wafers.²³ Figure 2(a) shows the previously reported fabrication process for the silicon membrane-supported μ -SOFC array by using only KOH wet etching,²⁰ and the process developed in this work by adding an additional step of short DRIE before the KOH wet etching is illustrated in figure 2(b). Only three membranes were drawn in a single window to illustrate the fabrication process. In the actual arrays, thousands of functional membranes were embedded in a single silicon membrane. The anisotropic KOH etching alone induced over-etched corners that make the edges of the square silicon membrane thinner as shown in figure 2(c), while with the additional DRIE circular trench, a tapered shape that is the thickest at the edges of the silicon membrane was established as highlighted by a red circle in figure 2(b).

Figure 2. Schematics of fabrication process for μ -SOFC array. (a) Without DRIE. (b) With DRIE (red circles point reinforced silicon supporting structure at the hetero-junctions). (c) Optical image of over-etched μ -SOFC array during KOH etching without DRIE.

In figure 2(b), μ -SOFC array reinforced by thicker silicon edge support was fabricated on a four-inch (100) double-side polished silicon wafer with thickness of 400 μm as a supporting substrate. The detailed process of creating the circular trenches to fabricate the electrolyte membrane arrays were similar to what was reported earlier.²⁰

The silicon supporting membrane was fabricated by first creating a 30 μm -deep trench using DRIE at the center of the exposed window to be etched with KOH solution, with a diameter that is 1.5 mm smaller than the edge length of the open window. Thin film YSZ electrolyte with thickness of 80 nm was deposited on the top side by atomic layer deposition (ALD) with the

condition similar to previously reported works.^{8, 13, 20} The silicon was then etched by through-wafer etching in 30 wt.% KOH aqueous solution at 85 °C to remove silicon until 20 μm-thick of silicon remained and the edge-reinforced silicon membrane for supporting the μ-SOFC array was created simultaneously. Afterward, Si₃N₄ was removed by reactive ion etching and 100 nm-thick nano-porous platinum was deposited on cathode and anode of the μ-SOFC array by radio-frequency (RF) sputtering with deposition conditions of 30 mTorr Ar pressure and 100 W RF power without a substrate heating. After deposition of platinum electrodes, each YSZ membrane became an individual fuel cell, and all individual fuel cells in the array were connected in parallel.

The fuel cell measurements were carried out by using μ-SOFC arrays with a diameter of opening on silicon membrane to be 3.6 mm. A total number of 2100 fuel cell membranes was embedded in this silicon membrane. The open circuit voltages (OCVs) and the I-V curves were characterized by an electrochemical potentiostat (Solartron 1470E, Solartron Analytical) at 350 and 400 °C with dry H₂ at the flow rate of 10 sccm as fuel and ambient air as oxidant. The thermal stability of the array was tested by performing 7 times of thermal cycling between 150 °C and 400 °C with two cooling and heating rates at 10 and 25 °C/min. The morphologies of the electrolyte membranes and the silicon membranes were characterized by field emission secondary electron microscope (FESEM, JEOL JSM-7600F) and optical microscope.

Anisotropic KOH etching without DRIE trench induced over-etched corners due to the different etching rates according to silicon crystallinity as shown in figure 2(c) and the over-etching introduced a feeble anchor at each corner which is highly vulnerable to mechanical and thermal impacts. Furthermore, a large amount of silicon residues underneath the electrolyte membrane remained and further etching to fully release the electrolyte membrane considerably

increases the risk of membrane failure. Unlike only anisotropic silicon etching for releasing the membrane, the addition of DRIE circular trench generated a new etched profile around the membrane as shown in figure 3. The newly created structure on the corners of array features a tapered and rounded silicon support, which further reinforces the silicon supporting membrane and silicon residues underneath the electrolyte membrane was fully removed.

Figure 3. Optical image of μ -SOFC array with DRIE after KOH etching.

Cross-section of silicon supporting structure with a FESEM image is illustrated in figure 4(a). The silicon support for the array consists of three different stage: A. (100) plane by anisotropic etching. B. tapered plane as a transition between (100) and (111) planes. C. silicon membrane for supporting 80 nm-thick YSZ membrane array. From the bottom view in figure 4(b), three-stage supports are also clearly observed. Especially, the tapered plane, B was evolved from the boundary of DRIE trench toward the etching window and figure 4(c) showed single cells in the

transition region between tapered plane and array support plane. The tapered edges play a role in fortifying the silicon supporting membrane structure on the anchor site, which reduced the chances of failure. Moreover, compared to conventional square μ -SOFC membranes, membranes in circular shape can evenly distribute the stress on the membrane and significantly reduce chances of breaking.¹⁷

Figure 4. Edge-reinforced μ -SOFC array structure. (a) Schematic of the cross-section of a μ -SOFC array with FESEM image. (b) Bottom view of the circular array taken by SEM. (c) Magnified view between tapered region and circular array region.

To verify the functional stability of a μ -SOFC array, OCV tests at 350 °C were performed over 30 hours as shown in figure 5(a). It is noteworthy that OCV was slightly fluctuated between 1.1 V and 1.05 V during initial 5 hours and stabilized at 1.03 V without OCV degradation and membrane failures. This result indicates that the membrane array is a defect-free and gas-impermeable structure. Figure 5(b) demonstrated anode and cathode sides of the cell after 30 hour OCV measurement and we observed no visible failures and degradations of the membranes. The polarization curves from the 2 mm μ -SOFC array measured at 350 and 400 °C are shown in figure 5(c). OCV values at 350 and 400 °C are slightly low below 1 V and the reason for this drop may be due to a sealing problem during fuel cell measurement, not the tested array structure itself. However, high peak power density of 317 mW/cm² was achieved at 400 °C and the power density converts to a total power output in the milliwatt scale (4.01 mW), which is rarely reported from nano thin film μ -SOFCs to date.^{6, 8, 20}

Figure 5. (a) The OCV stability monitoring for 30 hours with dry hydrogen as fuel and air as oxidant at 350 °C. (b) Optical images of both the cathode and the anode of the μ-SOFC array after 30 hours of OCV measurement, showing no broken membrane. (c) Polarization curves of the μ-SOFC array at 350 and 400 °C.

The thermal stability of a μ -SOFC array was also verified by repeating total 7 thermal cycling tests within a low operating temperature region. The μ -SOFC array was cooled down to 150 °C to avoid vapor condensation and heated up to 400 °C repetitively. From simple calculation based on mechanical properties of YSZ electrolyte,²⁴ a high thermal stress of 700 MPa was generated in the membrane during heating and cooling between this temperature range. As shown in figure 6(a), reproducible OCV values were obtained without any short circuit caused by membrane failure. Heating rate and cooling rate were both 10 °C/min and isothermal period during 5 min was imposed after heating or cooling to stabilize OCV. OCV was oscillated between 0.95 V and 1.08 V, exactly following to thermal cycles and, showing good OCV recovery close to the theoretical value at 400 °C. To introduce harsher thermal conditions on the cell, heating and cooling rates were increased to 25 °C/min and thermal cycles without an isothermal period were carried out consecutively. In figure 6(b), OCV was followed by thermal cycles and during the cooling, OCV was fluctuated between 0.89 V and 1.07 V. However, under the harsh thermal cycling, no visible membrane cracks and cell degradation were observed in the μ -SOFC array, indicating that the μ -SOFC array mitigates an abrupt thermal stress change from a rapid heating and cooling and shows excellent thermo-mechanical integrity of the array architecture.

Figure 6. OCV changes during thermal cycling tests between 150 °C and 400 °C with a dry hydrogen fuel. (a) OCV changes with moderate thermal cycles (10 °C/min). (b) OCV changes with harsh thermal cycles with steep heating and cooling rates (25 °C/min).

1
2
3 A silicon-based nano-thin film μ -SOFC electrolyte membrane array embedded in a silicon
4 supporting membrane with unique shape to ensure the thermal mechanical stability during cell
5 fabrication and operation was demonstrated by utilizing simple silicon micromachining
6 techniques. The silicon supporting membrane with thicker edges and corners was generated by
7 combining a DRIE and a KOH wet through-wafer etching of (100) silicon wafers. With the
8 dimension demonstrated, approximately 4 mW of total power output at 400 °C was obtained
9 from the array with 2 mm in diameter. The functional stability of the new array structure was
10 verified by maintaining high OCV value of 1.04 V at 350 °C for at least 30 hours, and the high
11 OCV recovered from the abrupt thermal cycling tests with fast heating and cooling rate of 25
12 °C/min also confirmed the superior thermal stability of the array. The new silicon supporting
13 membrane for μ -SOFC array application has provided an effective reinforcement for the fragile
14 nanometer-thin electrolyte membrane arrays. With the method reported here, the easy expansion
15 of the lateral dimension of the array beyond 6 mm can be expected, and with proper design and
16 layout of the cell array configurations, high total power output can be achieved for practical
17 applications of low temperature μ -SOFCs.
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

AUTHOR INFORMATION

Corresponding Author

*Email: peichensu@ntu.edu.sg

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors would like to thank the financial support from Tier 1 project (Grant No. RG92/13) and Tier 2 project (Grant No. MOE2013-T2-2-080), both from Singapore Ministry of Education.

REFERENCES

1. Steele, B. C. H.; Heinzl, A. Nature 2001, 414, (6861), 345-352.
2. Huang, H.; Nakamura, M.; Su, P. C.; Fasching, R.; Saito, Y.; Prinz, F. B. Journal of The Electrochemical Society 2007, 154, (1), B20-B24.
3. Kerman, K.; Lai, B. K.; Ramanathan, S. Journal of Power Sources 2011, 196, (5), 2608-2614.
4. Lai, B.-K.; Kerman, K.; Ramanathan, S. Journal of Power Sources 2011, 196, (4), 1826-1832.
5. Kerman, K.; Lai, B.-K.; Ramanathan, S. Advanced Energy Materials 2012, 2, (6), 656-661.
6. Tsuchiya, M.; Lai, B. K.; Ramanathan, S. Nat Nanotechnol 2011, 6, (5), 282-286.

7. Fan, Z.; An, J. W.; Iancu, A.; Prinz, F. B. *Journal of Power Sources* 2012, 218, 187-191.
8. Su, P. C.; Chao, C. C.; Shim, J. H.; Fasching, R.; Prinz, F. B. *Nano Lett* 2008, 8, (8), 2289-2292.
9. An, J.; Kim, Y. B.; Park, J.; Gur, T. M.; Prinz, F. B. *Nano Lett* 2013, 13, (9), 4551-4555.
10. Chao, C. C.; Hsu, C. M.; Cui, Y.; Prinz, F. B. *Acs Nano* 2011, 5, (7), 5692-5696.
11. Li, Y.; Su, P.-C.; Wong, L. M.; Wang, S. *Journal of Power Sources* 2014, 268, (0), 804-809.
12. Kim, Y. B.; Gur, T. M.; Kang, S.; Jung, H. J.; Sinclair, R.; Prinz, F. B. *Electrochemistry Communications* 2011, 13, (5), 403-406.
13. Su, P. C.; Prinz, F. B. *Microelectronic Engineering* 2011, 88, (8), 2405-2407.
14. Garbayo, I.; Pla, D.; Morata, A.; Fonseca, L.; Sabate, N.; Tarancon, A. *Energy & Environmental Science* 2014.
15. Evans, A.; Martynczuk, J.; Stender, D.; Schneider, C. W.; Lippert, T.; Prestat, M. *Advanced Energy Materials* 2015, 5, (1).
16. Evans, A.; Prestat, M.; Tolke, R.; Schlupp, M. V. F.; Gauckler, L. J.; Safa, Y.; Hocker, T.; Courbat, J.; Briand, D.; de Rooij, N. F.; Courty, D. *Fuel Cells* 2012, 12, (4), 614-623.
17. Baek, J. D.; Yoon, Y.-J.; Lee, W.; Su, P.-C. *Energy & Environmental Science* 2015, 8, (11), 3374-3380.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

18. Kerman, K.; Tallinen, T.; Ramanathan, S.; Mahadevan, L. *Journal of Power Sources* 2013, 222, 359-366.

19. Takagi, Y.; Lai, B.-K.; Kerman, K.; Ramanathan, S. *Energy & Environmental Science* 2011, 4, (9), 3473.

20. Su, P. C.; Prinz, F. B. *Electrochemistry Communications* 2012, 16, (1), 77-79.

21. Tang, Y.; Stanley, K.; Wu, J.; Ghosh, D.; Zhang, J. *Journal of Micromechanics and Microengineering* 2005, 15, (9), S185-S192.

22. Sato, K.; Shikida, M.; Matsushima, Y.; Yamashiro, T.; Asaumi, K.; Iriye, Y.; Yamamoto, M. *Sensor Actuat a-Phys* 1998, 64, (1), 87-93.

23. Pal, P.; Sato, K. *Micro and Nano Syst Lett* 2015, 3, (1), 1-42.

24. Srikar, V. T.; Turner, K. T.; Andrew Ie, T. Y.; Spearing, S. M. *Journal of Power Sources* 2004, 125, (1), 62-69.