<table>
<thead>
<tr>
<th>Title</th>
<th>A circular membrane for nano thin film micro solid oxide fuel cells with enhanced mechanical stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Baek, Jong Dae; Yoon, Yong-Jin; Lee, Wonyoung; Su, Pei-Chen</td>
</tr>
<tr>
<td>Date</td>
<td>2015</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10220/43701">http://hdl.handle.net/10220/43701</a></td>
</tr>
<tr>
<td>Rights</td>
<td>© 2015 The Author(s) (Royal Society of Chemistry). This is the author created version of a work that has been peer reviewed and accepted for publication by Energy &amp; Environmental Science, The Author(s) (Royal Society of Chemistry). 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: [<a href="http://dx.doi.org/10.1039/C5EE02328A">http://dx.doi.org/10.1039/C5EE02328A</a>].</td>
</tr>
</tbody>
</table>
A circular membrane for nano thin film micro solid oxide fuel cells with enhanced mechanical stability†

Jong Dae Baek,a Yong-Jin Yoon,a Wonyoung Leeb and Pei-Chen Sua*

We demonstrate a new architecture for a low temperature solid oxide fuel cell to enlarge the lateral dimension of the fragile nano thin film electrolyte from the micrometer to millimeter scale with greatly enhanced mechanical stability. The new structure was achieved by simple silicon micromachining processes to change the membrane shape from a square to a circle to reduce buckling-induced stress concentration that often caused membrane fracture. A tapered silicon membrane support with the thickest end of 30 μm was introduced as an effective membrane stress absorber. The new architecture effectively suppressed membrane buckling and decreased the maximum principal stress by 30–40%. The largest lateral dimension of the stable membranes was 3 mm in diameter, and the survival rate was significantly improved over square membranes having the same lateral dimension. Fuel cells with 100 nm-thick electrolytes showed stable open circuit voltages of 1.12 V at 400 °C for more than 8 hours without any membrane failure observed, showing the superior mechanical stability of the new cell architecture that is promising in the further practical applications of such devices.

Broader context
Solid oxide fuel cells (SOFCs) utilizing nanoscale thin film technology have effectively decreased their operating temperatures from typically required to be in the 800 °C to 1000 °C range to below 500 °C. With the help of silicon micromachining technology, such nanoscale thin film electrolytes were fabricated as free-standing membranes. However, in order to minimize the internal resistance of the cell, the membrane is usually made to be only a few tens of nanometers in thickness, and subsequently its mechanical stability is poor. The lateral dimension of a fuel cell determines the total power output of this device, and for nano thin film electrolyte SOFCs, enlarging the electrolyte to obtain higher power output without cracking the membrane becomes virtually impossible. In this work, we demonstrated a fabrication method for a new nano thin film SOFC architecture that can provide upward membrane scalability to obtain higher device power, and at the same time enhance the membrane mechanical stability for stable fuel cell operation.

Introduction
Micro-solid oxide fuel cells (m-SOFCs) using nanoscale thin film electrolytes are an emerging area for low temperature SOFCs operating at 300–500 °C.1–3 A dense and gas-impermeable electrolyte with sub-micrometer scale thickness has been demonstrated using thin film deposition techniques, including atomic layer deposition (ALD), pulsed laser deposition (PLD), and sputtering.4–11 Such thin film electrolytes are typically grown on silicon wafers12–14 or porous substrates, such as anodic aluminum oxide (AAO)15,16 as supporting substrates. However, since the deposition of dense and gas-tight electrolytes on a porous substrate with nanoscale thickness is challenging, a micro-machined silicon substrate remains a more practical architecture for m-SOFCs.

The fabrication of such free-standing electrolyte membranes on a silicon substrate has typically been done by performing through-wafer etching in KOH solution to release the membrane from the substrate.12–14,17 The resulting membrane geometry is either square or rectangular due to the crystallinity of the (100) silicon substrate (Fig. 1(a)), and such architecture for thin film SOFCs has been a common platform for the study of electrode or electrolyte materials in the literature. However, as the electrolyte is usually deposited at elevated temperatures (between 250 and 800 °C, depending on the deposition method), a compressive residual stress within the membrane is often observed.12–14,18 For instance, a highly compressive...
residual stress of \(-1100 \pm 150\) MPa was reported in a 300 nm-thick yttria-stabilized zirconia (YSZ) thin film deposited by PLD at 700 °C, and severe membrane buckling was also observed.\(^1\)

For sputtered YSZ deposited at room temperature, the residual stress was reported to vary from very compressive of \(-1400\) MPa to slightly tensile of 100 MPa, depending on the deposition parameters.\(^1\) Such high residual stress within the extremely thin electrolyte deteriorates its mechanical stability. Based on a Weibull analysis for brittle materials, the failure probability of a flat film increases exponentially with the geometric factor, \(L^3h\) for a square membrane, where \(L\) and \(h\) represent the lateral length and thickness of the membrane, respectively.\(^2\) In this sense, it is virtually impossible to further expand the lateral dimensions of the electrolyte membrane for higher total power output without causing membrane fracture. A typical lateral dimension for a 100 nm-thick, free-standing square membrane to have satisfactory mechanical stability is limited to 100 mm or less based on empirical experience.

The fracture of a membrane occurs when the maximum principal stress at any point within the membrane exceeds the tensile strength of the material (the Rankine criterion). For a membrane with higher compressive stress than the critical buckling stress, buckling occurs to relieve the compressive stress, and as a result, the fracture of a membrane can be avoided. Unfortunately, for a square electrolyte membrane, although buckling does reduce the magnitude of the stress, the asymmetric buckling pattern causes irregular membrane wrinkles, which induce high stress concentration points at the clamped edge. The buckling phenomena of square free-standing YSZ and yttria-doped barium zirconate (BYZ) electrolytes were reported both experimentally\(^3,4\) and computationally by Kerman et al., where they calculated the stress behavior of a square electrolyte membrane and concluded that the compressive stress within the membrane was indeed relaxed by buckling, but buckling-induced wrinkles, causing high stress concentration points at the clamped edges, also lead to membrane fracture.\(^5\)

It is known that a circular membrane has both a more uniform stress distribution under a static loading and a higher buckling resistance compared with a square membrane.\(^6,7\) Circular membranes have no geometrical discontinuities like square ones, such as 90° corners, to introduce high stress points by buckling and wrinkles.\(^8\) To date, only a few research groups have reported the fabrication of circular membrane electrolyte m-SOFCs, but either the fabrication process was too complex,\(^9,10\) or the membrane stability was poor with inferior fuel cell performance, due to electronic or gas leakages.\(^11,12\) A significant scaling up of a nano thin film circular electrolyte membrane with good mechanical stability has not been reported yet.

In this study, we demonstrate the fabrication of a circular nano thin film electrolyte for m-SOFCs with successful enlargement in the lateral dimension from the micrometer up to the millimeter scale. A simple two-step through wafer etching process was introduced, and the resulting cell architecture features a tapered edge support, acting as an effective stress absorber at the clamped edge of the membrane. Principal stress analysis was carried out using a finite element method (FEM) simulation to compare the mechanical stability of the square and circular membranes. The functionality and mechanical stability of the circular nano thin film SOFCs were verified by electrochemical measurements and statistical results of membrane survival rates.

**Details of experimental and computational study**

**Fabrication of circular electrolyte membranes**

A free-standing membrane on a single crystal silicon substrate can be fabricated by performing either through-wafer etching using wet chemicals to obtain a square membrane (Fig. 1(a)) or dry deep reactive ion etching (DRIE) (Fig. 1(b)) to obtain an arbitrary shape of interest.\(^13,14\) The latter requires sophisticated DRIE equipment with 4 to 5 hours of etching time to process each wafer, and therefore is not practical for the batch production of thin film SOFCs.

The fabrication process of our new architecture for a circular membrane combined both anisotropic wet etching and DRIE (Fig. 1(c)). A first DRIE short etching is applied to pre-define a
circular shape, and the etching depth is a few tens of micrometers out of the total 400 μm etching depth. A second KOH wet etching was then applied to continue and complete the through-wafer etching and release the membrane. The shape of the resulting through-hole created by the combinatorial etching is circular, with a thin tapered silicon ring along the edge of the membrane. The details of the overall fabrication process and the tapered silicon edge support can be found in the ESI† (Fig. S1 and S2).

Deposition of thin film electrolyte membranes

The electrolyte thin films were prepared by two deposition methods, ALD and PLD, for two different electrolyte materials, YSZ and BYZ, respectively, to obtain different residual stresses for the stability test of our cell structure. 100 nm-thick YSZ was deposited by ALD at 250 °C of substrate temperatures and with a recipe similar to previously reported work.21,33–35 100 nm-thick BYZ was deposited by PLD (Coherent 248 nm KrF excimer laser, 2.5 J cm−2, 3 Hz, 1 Pa O2) at a substrate temperature of 800 °C.

FEM study for stress analysis

The principal stress distributions within the membrane were computed using a FEM simulation to confirm the stress distribution within the square and circular YSZ membranes. A commercial software package (COMSOL Inc.) was used to identify the highly stress-concentrated regions on the membranes under a clamped boundary condition. To simplify the modeling, the YSZ electrolyte was modeled as a linear elastic and isotropic material. The three different membrane models shown in Fig. 1 were constructed to investigate the effect of membrane shape and tapered edge support on the mechanical stability, namely:

(i) A 2 mm × 2 mm square membrane clamped at the edge,
(ii) A circular membrane with a diameter of 2 mm clamped at the edge, and,
(iii) A circular membrane with a diameter of 2 mm and a tapered edge support of 450 μm in width.

To simulate the fuel cell operating conditions, 5 psi of static pressure difference on the bottom side and 400 °C of operating temperature were applied in the calculation. The material properties of YSZ and silicon substrates for the numerical simulation were obtained from the literature.36 Maximum principal stresses in the films were assessed using non-linear large-deflection theory because the deflections were expected to be non-trivial with respect to the membrane thickness. A compressive in-plane strain was applied to simulate the residual stress in the initial configuration as \( s_0(1 - v)/E \), where \( s_0 \), \( v \), and \( E \) represent the residual stress of a thin film, Poisson’s ratio, and Young’s modulus, respectively, and a compressive stress of 500 MPa was preloaded. In this calculation, we only examine the stress distribution without letting buckling occur.

Fuel cell characterization

m-SOFCs with circular electrolytes were prepared by depositing 100 nm-thick nano-porous Pt electrodes on both sides of the circular electrolyte. The m-SOFC was clamped on a custom-built cell chamber placed inside a tube furnace for measurements. Pure dry hydrogen at a flow rate of 10 sccm was fed at the anode side while the cathode side was opened to ambient air for the oxygen source. A gold-coated titanium probe attached in a micro-manipulator was in contact with the cathode side for current collection, and the anode was electrically connected to the chamber via the Pt electrode. The test chips were heated at 5 °C min⁻¹ to the desired operating temperature. A potentiostat (Bio-Logic, SP-200) was used to obtain current–voltage (I–V) characteristics. The film thickness, morphologies, and membrane deflections were examined using a field emission secondary electron microscope (FESEM, JEOL JSM-7600F, operating voltage 15 kV) and an optical microscope (OM).

Results and discussion

Free-standing circular membrane architecture

The OM images of the fabricated circular electrolyte membrane architectures are shown in Fig. 2. The transparent circles on the
silicon chips (Fig. 2(a)) are the 100 nm-thick free-standing electrolyte membranes with diameters from 500 nm to 3 mm. Circular membranes with diameters up to 6 mm were also fabricated, but the survival rate was low, around only 15%, and thus the 3 mm diameter membrane, which had a more than 50% survival rate, was taken as the largest mechanically stable dimension with this architecture.

As shown in Fig. 2(b), buckling deformation, caused by a compressive residual stress, was also observed in the circular membranes for both ALD-YSZ and PLD-BYZ but was much less severe than with the square ALD-YSZ membrane. In terms of the buckling-induced wrinkles at the clamped edge(s), many wrinkles were presented in the square membrane, whereas no apparent wrinkle was observed in the circular ones. From Kerman’s calculation, such buckling-induced wrinkles at the clamped edges are stress concentration points where the fracture of membranes usually occurs. Here, by changing the membrane from square to circular, the buckling-induced wrinkles were minimized and the chances of membrane fracture were expected to decrease significantly.

Fig. 2(c) shows the membrane, viewed from the bottom side of the silicon chip, with a schematic of the cross-section. The membrane-supporting structure has an additional tapered support (portion B) between the major support (portion A) and the free-standing nano-thin electrolyte membrane (portion C). The tapered edge support is a thin and annular single crystal silicon with approximately 450 nm in width and 30 nm in height, where the exact dimensions can vary depending on the process and design parameters.

The addition of this thin taper-shaped support is the key to the success of scaling up the nano thin film electrolyte because this thin support serves as a stress absorber to effectively reduce the stress concentrated at the clamped edge.

FEM calculation for membrane stress distribution

The stress distributions within the nano thin film electrolyte were calculated by FEM to evaluate the effectiveness of the tapered edge support in relieving stress in the membranes. The calculation results of principal stress distribution (Fig. 3(a–c)) demonstrate a much more uniform stress distribution across the circular membrane with a tapered edge support (Fig. 3(c)) than either the square membrane (Fig. 3(a)) or the circular membrane without a tapered edge support (Fig. 3(b)). The maximum principal stress was 1.4 GPa in a clamped square membrane, 1.2 GPa in a clamped circular membrane, and 0.8 GPa in a clamped circular membrane with a tapered edge.

![Fig. 3 Principal stress distributions on clamped circular and square membranes. (a) Square YSZ membrane with a lateral length of 2 mm. (b) Circular YSZ membrane with a diameter of 2 mm. (c) Circular YSZ membrane with a diameter of 2 mm and a tapered edge support of 450 nm in width (black arrows point to the highest stress regions on the membranes). The thickness of the membranes is 300 nm in all cases. (d and f) Circular YSZ electrolyte with a diameter of 2.8 mm and the square YSZ electrolyte with a width of 2.9 mm broken during fuel cell tests (red arrows point to the approximate regions of initiating membrane failure).](image-url)
support. Compared with the clamped square and circular membranes, the circular membrane with a support showed a 30–40% reduction in the maximum principal stress. That is, the maximum principal stress of the circular membrane, located at the clamped edge(s), was reduced significantly by changing the membrane shape from square to circle, and reduced further by introducing the tapered edge support.

Fig. 3(d–f) show the corresponding fractured thin film m-SOFCs with structures in Fig. 3(a–c) after the fuel cell test, which is a good indication of where the fractures in the membrane initiated. For the square membrane and the circular membrane without a tapered support, the fracture was initiated at the clamped edge, where the stress is the highest, as confirmed by our simulation results. On the other hand, for the circular membrane with a tapered edge support (Fig. 3(f)), the fracture was initiated near the membrane center because the fragments of the fractured membrane were still clamped along the circular boundaries. This is also in agreement with the FEM calculation results that the highest stress was at the center of the membrane. Therefore, the tapered edge support effectively restrained the edge-fractures typically observed in square membranes and accordingly, mechanical stability was maintained during fuel cell operation.

Electrolyte functionality by fuel cell measurement

The mechanical stability of the new cell architecture was further explored by open circuit voltage (OCV) measurements.

Membrane survival rates

The enhanced mechanical stability of the tapered edge-supported circular membranes was further quantified with the membrane survival rate (percentage of membranes surviving after the fabrication process), as shown in Fig. 4. The survival rates for different membrane lateral dimensions between square and circular membranes were compared by counting a total of 144 cells with 12 cells for each size.

As expected, the survival rates decreased as the membrane size increased for both membrane shapes, as reported by Kerman et al.22 More importantly, the circular membranes showed higher survival rates than the square membranes over all membrane sizes. For the largest fabricated YSZ membranes with 3 mm of lateral dimension, none of the square membranes survived, while 50% of the circular membranes remained intact. These results provide statistical evidence of the enhanced mechanical stability of our new circular cell architecture over the widely reported square structure.

Fig. 4 Comparison of survival rate between the fabricated circular and square YSZ membranes showing the better survival rate of the circular membranes. A total of 12 cells were compared for each lateral dimension.

Fig. 5 (a) OCV evolution of the circular Pt/YSZ/Pt and Pt/BYZ/Pt fuel cells at 400°C for 8 h with dry H2 as a fuel. Polarization curves obtained from (b) a Pt/YSZ/Pt m-SOFC (c) a Pt/BYZ/Pt m-SOFC at 350°C (blue) and 400°C (red).
As shown in Fig. 5(a), the OCVs for YSZ and BYZ fuel cells achieved high values of 1.07 V and 1.12 V, which are close to the theoretical OCVs of 1.127 V at 400 °C with pure hydrogen fuel and air as the oxidants, and OCVs were stable for over 8 h, with less than 10 mV decay in both fuel cells. The high and stable OCVs over time provide direct evidence that the circular template developed in this study works as good as previously confirmed square templates.

Fuel cell performance measurement using the 1.5 mm diametrical circular YSZ m-SOFC and the 1.6 mm diametrical circular BYZ m-SOFC was conducted at 350 °C and 400 °C in a low temperature region (Fig. 5(b and c)). At 400 °C, YSZ and BYZ cells showed maximum power density of 437 mW cm⁻² and 76 mW cm⁻² and the corresponding total power output of 7.72 mW and 1.53 mW, respectively. The total power output has increased from typically microwatt scale to milliwatt scale, which has never been observed in a single free-standing m-SOFC membrane.

**Conclusions**

We have successfully fabricated nano thin film m-SOFCs with a circular membrane having a tapered thin edge support to effectively enhance the mechanical stability of the nanoscale membrane. The center-symmetric geometry of the circular thin film helped to distribute the stress of the membrane uniformly in the radial and circumferential directions, and the tapered edge support served as a stress absorber and significantly suppressed the high magnitude of stress at the clamped edges. The addition of the tapered edge support created along the circular boundary was reduced by 30–40% of the maximum stress at the clamped edge of the membrane, and accordingly reduced the risk of membrane fracture. The membrane survival rates provided statistical evidence for enhanced mechanical stability of the membrane using the new fuel cell architecture, and subsequently enabled scale-up of the m-SOFC to millimeter size and substantial improvement of the total power output. The stable OCVs over 8 h and good power density achieved by ALD-YSZ at 400 °C also justified the better mechanical stability and functionality of the circular thin film electrolytes to be dense and pinhole-free in this cell-supporting structure. Thus, the new cell architecture presented in this work can be a promising template for large-scale nano thin film SOFCs to achieve higher total power output with mechanical and functional stability.

**Acknowledgements**

The authors acknowledge financial support by Tier 1 Grants (M4010998) and Tier 2 Grants (M4020202), both from the Singapore Ministry of Education (MOE), and by the Basic Science Research Program (NRF-2014R1A1A0509845) and the Global Frontier R&D Program on Center for Multiscale Energy System (NRF-2014M3A6A7074784), both from the National Research Foundation of Korea. The authors also thank Yong Li for deposition of PLD-BYZ, and Kang Yu Liu and Chen-Chiang Yu for the deposition of ALD-YSZ.

**Notes and references**