Toward the Miniaturization of Solid Oxide Fuel Cells

by Enrico Traversa

Sustainable energy production, compatible with environment preservation, is one of the major problems to be tackled in the near future. The search for new energy production technologies as alternatives to fossil fuel combustion need to consider renewable sources. Fuel cells show potential because, depending on the type of fuel cells, they can be used not only for the production of stationary energy (mainly solid oxide fuel cells, or SOFCs), but also for mobile applications for vehicles and portable electronics (mainly polymer electrolyte fuel cells, or PEFCs). However, recently it has been demonstrated that SOFCs can be also used for mobile applications and are expected to produce energy densities per volume and specific energy per weight significantly larger than PEFCs and state-of-the-art rechargeable Li-ion and Ni metal hydride batteries. This article focuses on recent developments in the miniaturization of SOFCs, with a critical review of the obstacles to be overcome.

Scaling-Down SOFCs

Solid oxide fuel cells (SOFCs) find their main exploitation in stationary energy production applications with power output in the 1 kW to 1 MW range, as described in a companion article in this issue, which require a scale-up of their features. However, the large energy densities of SOFCs and the versatility in fuel use, not limited to hydrogen, generated interest in the deployment of micro-SOFCs (μ-SOFCs) for mobile power generation in the lower 1-500 W range. Foreseeable applications include portable electronic devices (which are now powered by rechargeable batteries), vehicle power supplies, and auxiliary power units.[1-3]

Fuel cell systems for compact, portable applications have great potential to achieve significant market penetration because of the high cost of the batteries they will replace on a $/W-hr/kg basis. Moreover, SOFCs are expected to produce energy densities per volume and specific energy per weight significantly larger than state-of-the-art rechargeable Li-ion and Ni metal hydride batteries, and larger also than polymeric electrolyte membrane fuel cells (PEMFCs), especially when hydrocarbon fuels will be used.[4] This feature is crucial because the ever increasing functionalities offered by modern portable electronic devices soon will increase energy requirements to a level that cannot be sustained by rechargeable batteries without increasing their size or sharply reducing their running time.[5,6] A further advantage with respect to rivaling batteries is the continuous SOFC operation when fed with fuel and oxidant, compared to the charge-discharge cycling operating mode of batteries.

Because direct conversion of chemical energy into electrical energy does not suffer from the thermodynamics efficiency restrictions of conventional thermo-mechanical energy production methods, in principle it is possible to scale down to the micrometer level the size of the whole device without affecting the SOFC overall efficiency.

Reduction of SOFC operating temperatures is a prerequisite for their use in portable devices, targeting the 300-600°C temperature range.[7-9] To achieve the objective of these low operating temperatures, new materials, processing, and unique architectures must be developed and re-examined. Two are the most successful designs so far, which will be described in the following paragraphs, for fabricating SOFCs for portable applications at lower operating temperatures. These are the micro-tubular SOFC design, which allows scaling down the SOFC size at the millimeter range, and the thin-film design of SOFCs prepared on silicon substrates using microfabrication technologies, which allows scaling down the SOFC size at the sub-millimeter range.

Micro-Tubular SOFCs

Micro-tubular SOFCs have been reviewed in a very recent paper.[10] The main limiting factor for using SOFCs in portable power production was the high operating temperature and the bulky design, which hindered a fast start-up, indeed a necessary requirement to compete with engines and batteries. The development of a micro-tubular SOFC stack based on extruded zirconia tubes with a wall thickness of 0.2 mm and an internal diameter of 2 mm circumvented this limit, allowing rapid thermal cycling between 400 and 800°C at a rate of 200°C min⁻¹ without failing, due to the cell robustness.[11] Later, tolerance to thermal cycling at a much faster heating rate of 4000°C min⁻¹ has been demonstrated.[12] Despite limited power generated, these promising findings boosted research activity to improve micro-tubular SOFC materials performance, processing, and cell and stack design.

The most customary stack design of micro-tubular SOFCs is a heat exchanger-like design, with a bundle of micro-tubular SOFCs with hydrogen flowing inside each cell and air flowing outside the cells. Therefore, whereas in planar SOFCs where sealing is critical, tubular SOFCs only need sealing at the junction with cells and manifolds. However, due to their tiny dimensions, micro-tubular SOFC sealing needs to be more accurate than for the larger counterparts, even though the literature on this topic is scarce.[13]

The research in the field of micro-tubular SOFCs has followed the same patterns pursued for reducing the operating temperature of large-scale SOFCs.[14] Micro-tubes of alternative electrolytes, such as Gd-doped ceria (GDC) and Sr- and Mg-doped lanthanum gallate (LSGM) have been extruded,[15] but their mechanical properties are inferior to those of yttria-stabilized zirconia (YSZ) tubes, in particular their toughness. A critical factor in reducing the Ohmic resistance is the reduction of electrolyte thickness using anode-supported thin film electrolytes in tubular configuration,[16] following the research trends of planar SOFCs. Ni-YSZ tubes were extruded and YSZ electrolyte layers were deposited by dip-coating in a YSZ slurry in the approach followed at the University of Connecticut. They have also developed an original stack design, where single micro-tubular SOFCs are aligned to form planar multi-cells arrays, which can be subsequently stacked as they were planar cells.[17] The cells were connected to the current collectors by brazing with silver. The power density output for the stack at 850°C fueled with hydrogen was almost 60 mW cm⁻², showing that further progresses are possible.

A different processing procedure using electrophoretic deposition (EPD) has been proposed by the Alberta Research Council in Canada to fabricate one-end-closed anode-supported single cells.[18] EPD is a very versatile technique that shows advantages for the fabrication of ceramic multilayers for SOFCs.[19,20] A graphite rod was used as a substrate to sequentially deposit by EPD anode (Ni-YSZ), electrolyte (YSZ), and cathode (LSM) layers. However, large overpotential losses at the cathode avoided to obtain a large power density output.[18]

In an approach proposed by the National Institute of Advanced Industrial Science and Technology (AIST) and the Fine Ceramics Research Association (FCRA) of Nagoya, Japan, under the frame of their joint research funded by NEDO, anode-supported electrolyte YSZ was substituted with GDC.[21] NiO-GDC tubes were prepared by extrusion and

the GDC electrolyte layer was prepared by dip-coating.[22] This group developed a completely different design for the stack, consisting of a cube-shaped array of micro-tubular cells distributed in a porous matrix made of the cathode material.[23] The first demonstration showed the fabrication of a 3 cm x 3 cm x 3 cm cathode matrix cube with 36 micro-tubular cells 2 mm in diameter, arranged in a 6 x 6 configuration.[23] The group has worked intensively toward the reduction in size of the micro-tubular SOFCs, reaching needle-type cells where the tube diameter was 0.4 mm.[24] Figure 1 shows a photo of a micro-tubular SOFC bundle with the size of 1 cm³ made of 25 micro-tubular cells with the diameter of 0.8 mm in a 5 x 5 configuration. The tubular cells are based on anode-supported GDC electrolyte and were stored in a porous LSCF matrix. The electrode area of the single bundle reaches over 5 cm². The electrochemical performance has been also improved with time; the power density obtained for a single micro-tubular cell 0.8 mm in diameter increased from 350 mW cm⁻² at 550°C with hydrogen as a fuel[21] up to more than 1 W cm⁻² upon improvement of the anode microstructure.[25] This led to an overall volumetric power density output of 2 W cm⁻³ at 550°C with hydrogen for a module of the size of 0.2 x 1 x 3 cm, consisting of a stack of three bundles with fuel manifolds, each bundle having five micro-tubular cells.[26] Further improvement has being searched through the use of bilayer electrolytes,[27,28] to block the electronic conductivity of GDC.[29,30]

In summary, even though there are already a few commercial products based on micro-tubular SOFCs in the market, there is still a lot of space for improvement of electrochemical performance through study and design of materials and their processing,[31] in particular to reduce polarization losses at the electrodes, and on stack design.

Thin Film µ-SOFCs

Thin film µ-SOFCs based on silicon substrates with lateral dimensions in the sub-millimeter scale are very promising for use in portable electronic devices operating at low temperatures. The integration of thin film SOFC materials with silicon technology takes advantage of recent progresses in creating complex 3D structures utilizing a variety of micromachining techniques.[32] Moreover, a microfabricated fuel cell could, in principle, be integrated onto a single chip with other electronic circuits, enabling extended, remote operation of electronic devices.[33]

While several papers have been reported on the investigation of thin film materials for µ-SOFCs, which have been recently reviewed,[34,35] less numerous works have been reported on the fabrication of the entire µ-SOFC device, being the market still far. Nonetheless, the reported preliminary results are very promising.

The first example of a thin film µ-SOFC was probably reported by the University of Houston.[36] The development of the fuel cells followed an original strategy: a thin-film electrolyte, either YSZ or Sm-doped ceria (SDC), was grown by pulsed laser deposition (PLD) on a nickel foil substrate and then photolithographic patterning and chemical etching were used to develop pores in the anode for gas transport. A porous LSC cathode layer on the electrolyte side and a porous NiO-YSZ layer on the porous Ni side to boost the anode triple phase boundary were deposited by PLD to complete the cells. The maximum power density of 140 mW cm⁻² at 575°C was obtained for cells with YSZ electrolyte, using hydrogen as fuel.[37] The approach of using Ni substrates for the µ-SOFC fabrication has been reported also by other groups, achieving lower power density outputs.[32,38,39]

A research effort at MIT showed the first example of using silicon processing technologies developed for microelectromechanical systems (MEMS) applied to the fabrication of free-standing SOFC electrolyte membranes.[40] As shown in the schematics in Fig. 2, the design is based on a conventional dual-chamber configuration where the dense, free-standing electrolyte membrane acts as air/fuel barrier and mechanical support for anode and cathode layers. Figure 2 reports also an example of a cell fabricated at the University of Rome Tor Vergata, with SEM-micrographs of a bottom view of the free-standing cell and of the cross-section.[41] One of the most important problems to be tackled for µ-SOFC fabrication is their thermal-mechanical stability. Residual tensile or compressive stresses deriving from thermal expansion mismatch with the substrate (SiN$_x$, for instance) can result in buckling and/or failure of the free-standing membrane, even at relatively low temperatures. It has been found that the deposition technique affected the residual stress in the electrolyte films.[40] Only µ-SOFCs with larger thickness/area ratios, thus with an unfavorable electrochemical design, achieved an average fracture temperature significantly above their operating temperature.[40]

The use of Foturan, a photo-curable glass ceramic that can be micromachined by HF etching, has been proposed by ETH Zurich as a µ-SOFC substrate alternative to silicon, since its thermal expansion coefficient match well with the SOFC materials used.[4] The maximum power density of 150 mW cm⁻² with open circuit voltage of 1.06 V was measured at 550°C using hydrogen as fuel on a cell with a sputtered platinum anode, an electrolyte prepared by two YSZ layers, one prepared by PLD and the other by spray pyrolysis, and a platinum paste cathode.[4]

Ultrathin µ-SOFCs were fabricated at Stanford University using microfabrication techniques (lithography and etching), made of a YSZ electrolyte film as thin as 50 nm deposited by rf sputtering on a silicon wafer, with porous Pt films both for anode and cathode prepared by dc sputtering.[42] The power density obtained was outstanding: the power output using hydrogen as fuel of a cell with a 50 nm-thick YSZ electrolyte was 130 mW cm⁻² at 350°C. Moreover, the addition of a supplementary layer of GDC between the YSZ and cathode films increased the power output up to 200 mW cm⁻² at 350°C, reaching 400 mW cm⁻² at
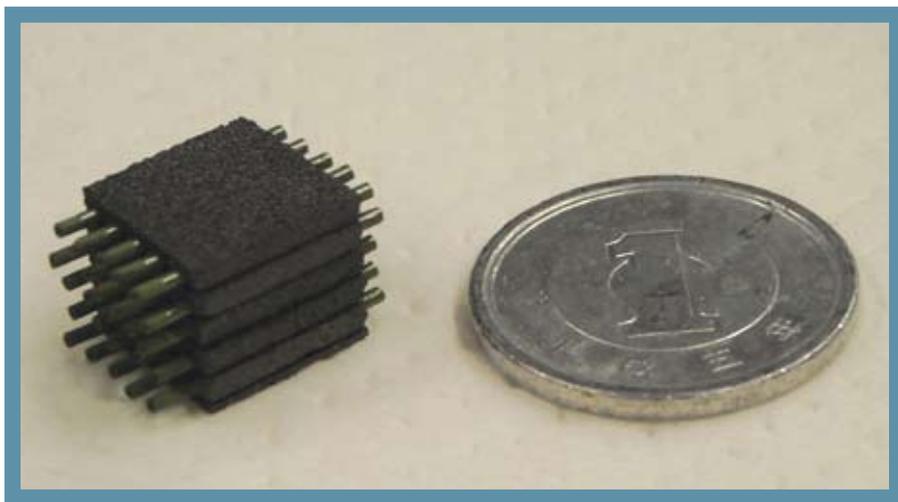
Fig. 1. *Micro-tubular SOFC bundle with a size of 1 cm³, jointly developed by the National Institute of Advanced Industrial Science and Technology (AIST) and the Fine Ceramics Research Association (FCRA) of Nagoya, Japan; 25 micro-tubular cells, each with a diameter of 0.8 mm and based on anode-supported GDC electrolyte, were housed in a porous LSCF matrix. The electrode area of the single bundle reaches over 5 cm². (Photo courtesy of Toshio Suzuki, AIST, Advanced Manufacturing Research Institute, Functional Assembly Technology Group, Nagoya, Japan.)*
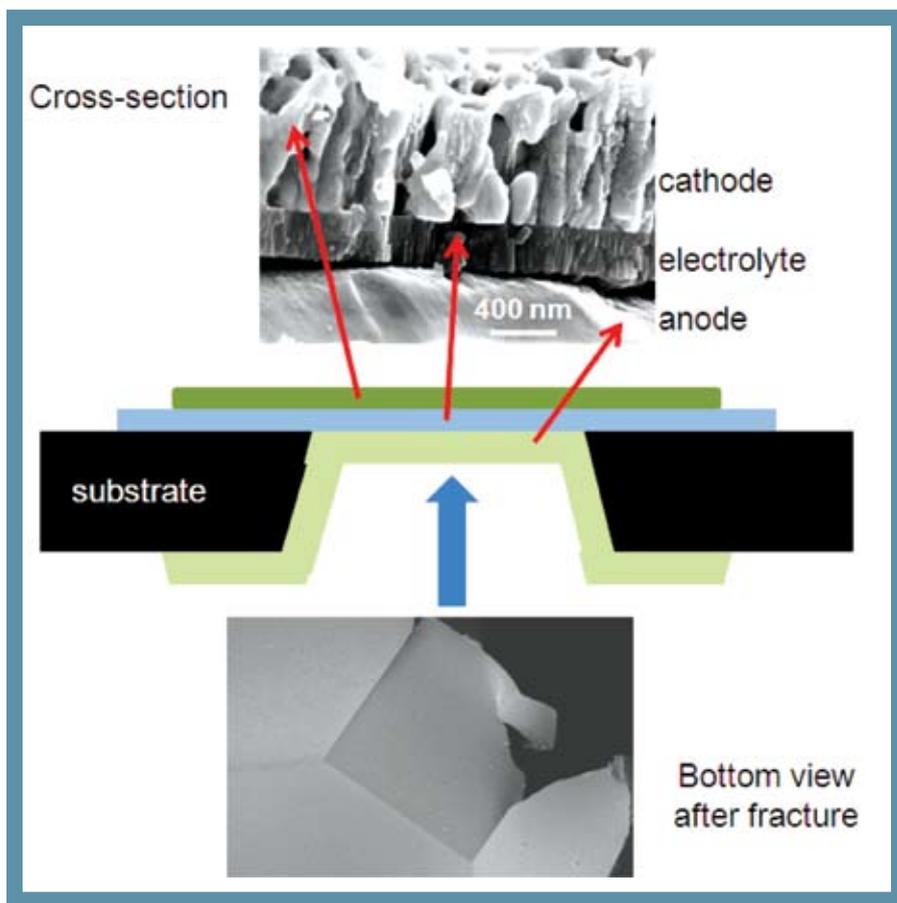
Fig. 2. *Schematic diagram of the design of microfabricated μ-SOFCs based on a free-standing electrolyte membrane with anode and cathode layers, together with SEM micrographs of the bottom view and the cross-section of a SOFC, fabricated at the University of Rome Tor Vergata. The electrolyte is SDC and the electrodes are made of Pt. The size of the cell is 0.25 mm (bottom view).*

400°C. Other groups fabricated similar μ-SOFC devices, but the power output was unrivaled. For instance, at Harvard, using a cell of similar configuration with a 100 nm-thick YSZ electrolyte, the maximum power density was 90 mW cm^{-2} measured at 500°C, and even substituting Pt at the cathode with $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ (LSCF) led to a maximum power density of 60 mW cm^{-2} at the same temperature.[43] LSCF should have much lower overpotentials than Pt at low temperatures, although recent findings showed that removing Si at the Pt/YSZ interface dramatically improve the electrochemical performance,[44] and this might be a possible explanation for the Stanford results.

Simulation studies have determined that thermal-mechanical reliability of μ-SOFCs can be improved using corrugated membranes that can reduce thermal stresses.[45] The group of Stanford was able to fabricate a μ-SOFC with a corrugated electrolyte membrane almost doubling indeed the power output: both flat and corrugated Pt/YSZ/Pt cells had a projected area of 0.0036 cm^2 (600 μm × 600 μm), and the depth of cups in the corrugated membrane was 20 μm, showing a maximum power density of 680 mW cm^{-2} at 400°C, with respect to that of 360 mW cm^{-2} for the flat membrane.[46]

A further step forward is represented by the μ-SOFC system developed under the frame of the ONEBAT Swiss project, which consists not only in a μ-SOFC device,[4] but also in the gas-processing unit for fuel reforming and post-combustion, together with a suitable thermal management system.[3] The most important output of this work is the demonstration of the technical feasibility of such kind of a system, which can become competitive once the SOFC performance will be enhanced through materials improvement.

Materials Challenges for Thin Film μ-SOFC Development

The progress that has to be made for boosting the performance of thin film μ-SOFCs concern both electrolyte membranes and electrodes with low overpotentials, especially the cathode. For instance, depositing epitaxially-ordered electrolyte films will improve their ionic conductivity with respect to polycrystalline films and will have also a beneficial effect on thermal-mechanical reliability. We recently discovered that epitaxially-grown SDC single crystals are stable in low oxygen partial pressure environments, while the equivalent polycrystalline films were dramatically

unstable.[47] This is a caution for use in μ-SOFCs and the ability to produce crystalline-ordered electrolyte films might be advantageous for practical applications. The cathode selection and fabrication can be the real crucial point for μ-SOFC development. However, a recent paper demonstrated that PLD can be used to fabricate nanoporous perovskite-type cathodes having low area specific resistance, and this is very promising for further developments.[48] ■

About the Author

ENRICO TRAVERSA is Principal Investigator at the International Research Center for Materials Nanoarchitectonics (MANA) at the National Institute for Materials Science (NIMS), Tsukuba, Japan, leading a group on Nanomaterials for Fuel Cells since January 2009. He joined the University of Rome Tor Vergata in 1988 where he is currently Professor of Materials Science and Technology. He is Senior Vice-Chair of the ECS High Temperature Materials Division. Dr. Traversa's research interests are in nanostructured materials for environment, energy, and healthcare, with special attention to solid oxide fuel cells. He is author or co-author of seven patents, more than 400 scientific papers (more than 230 of them published in refereed international journals), and edited sixteen books or special issues of journals. Elected in 2007 in the World Academy of Ceramics, he is currently Associate Editor for the *Journal of Nanoparticle Research* and *Science and Technology of Advanced Materials*. He may be reached at traversa.enrico@nims.go.jp.

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