

# A review on high power SOFC electrolyte layer manufacturing using thermal spray and physical vapour deposition technologies

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**Abstract** Manufacturing of solid oxide fuel cell (SOFC) components remains nowadays a key point for the industrial development of this technology. Especially, the deposition of the dense electrolyte layer which is sandwiched between the porous anode and the porous cathode is of paramount importance and thus focuses a lot of attention. Therefore, this paper considers and reviews recent developments concerning solid electrolyte layers manufacturing using thermal spray (TS) and physical vapour deposition (PVD) technologies.

**Keywords** Solid oxide fuel cell (SOFC) · Solid electrolytes · Thermal spray (TS) · Physical vapour deposition (PVD)

## 1 Introduction

In the frame of the general concern about global warming of our planet following the intensive use of fossil fuels during the 20th century, many studies were initiated in the 1990's in order to find solutions for replacing the use of these fossil fuels by other renewable energy sources. Of course the challenge is not easy and if electricity certainly appears as the ultimate solution, it is not applicable immediately on a broad basis, especially for mobile applications, due to the low energy density of actual storage solutions.

Therefore, intermediate solutions have certainty to be developed among which are the “promising” fuel cells, especially when fed with hydrogen. Hydrogen distribution

being nevertheless another challenge, the development of fuel cells able to use hydrocarbon fuels as well as hydrogen remains of great interest. Therefore, many research works were and still are devoted to the development of the so called solid oxide fuel cell (SOFC) which would fulfil the aforementioned property.

While prototype scale productions were achieved in several companies or institutions during the past 20 years, the actual situation is that the way to industrial scale production of high power fuel cells remains uncertain essentially due to the high production costs and limited life time of these devices. Schematically, high production costs are linked to time consuming manufacturing techniques while limited life time is linked to the high working temperature of the cells inducing failures due to thermal stresses and interdiffusion processes. Thus, the main actual trends in research are oriented both towards the development of solid electrolyte layers with higher ionic conductivity and/or lower thickness in order to be able to reduce the working temperature of the cells and towards the development of mass production techniques avoiding the high temperature sintering steps of green ceramics. Of course, the fabrication of the other parts of the cells such as the electrodes and the interconnectors also present some challenges but this paper will only review and discuss some recent results obtained implementing thermal spray (TS) and vapour phase deposition techniques in order to produce thin and tight electrolyte gas layers for large size fuel cells.

Although a number of “exotic” compositions have been found which present higher ionic conductivity than yttria stabilized zirconia (YSZ), a number of drawbacks such as lower stability under reducing conditions, undesired phase transformations or interaction with cathode or anode materials do not seem to let them much chance to supersede YSZ by SOFC electrolyte material [1]. Therefore,

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most of the following discussion will refer to the deposition of YSZ based electrolyte layers.

## 2 State of the art

General structure of SOFC as well as details about their development history will not be reported here as they may be found in many papers such as that of Badwal and Foger [2], Huijsmans et al. [3] or Appleby [4]. In the same way we shall not consider the subject of the chemical composition of the materials which has also been discussed by many authors such as McEvoy [1] or Ebrahimi [5]. Let's only recall that the first industrial prototypes of SOFC for civil applications appeared in the 1980's (Westinghouse, Sulzer-Hexis) and that despite significant on site experimentations in several countries [6], no significant industrial production stage has yet been reached.

Concerning the electrolyte production, a number of techniques have been considered from the beginning of the intensive study of SOFC in the 1980's [7]. Some of them are simple and robust such as tape casting, and others allow to use a variety of precursor materials such as chemical vapour deposition (CVD) but none of them propose altogether a high deposition rate, smooth and dense layers, low capital expenditure, robustness and may be above all a low process temperature. Given the actual objective to produce fuel cells with a working temperature in the range 650 °C–700 °C, allowing particularly using metallic parts, it is of primary importance to avoid high temperature production steps such as sintering. Therefore, low temperature techniques such as TS and physical vapour deposition (PVD) receive more and more attention from the research community.

As TS allows producing deposits of virtually any kind of materials (metals, ceramics, polymers,...) and any mixture thereof at high deposition rates, and also to some extent allows to tailor the porosity of the deposited layers, it was among the first surface engineering techniques to be implemented [8–13] for the production of prototype SOFC components.

PVD techniques, their lower deposition rate and the difficulty to master the deposit composition were considered more recently, but they receive more and more attention given the possibility which is offered to create very thin layers.

## 3 TS

TS is a technique by which ceramic powder particles are melted in a high temperature gas jet and propelled by this gas jet towards a substrate where they eventually form a

layer by the addition of a number of splats produced by the deformation of each individual particle upon impact. Thus the generic structure of a ceramic layer formed by TS is, as shown in Fig. 1, composed of microcrystalline ceramic lamellae more or less attached together and separated by voids and cracks. Of course, such a structure is hardly gas tight and, if standard practice powder particles are used, e.g., 50 µm to 100 µm in diameter, the layer cannot be very thin and often requires some post treatments in order to eliminate voids and cracks [13]. Such post-treatments when operated at high temperature will often result in undesirable chemical interactions such as the growth of a high resistance  $\text{La}_2\text{Zr}_2\text{O}_7$  layer at the interface between YSZ and lanthanum strontium manganite (LSM) often used as electrode material [14]. In addition, this type of building process also introduces structural heterogeneity which results in anisotropy in the ionic conductivity, the through thickness value being only about 50% of that measured parallel to the surface due to the high number of interfaces [15].

The technique must then be adapted bearing in mind that it is not easy to reduce the size of the powder particles because the flow ability of the powder, which is an essential property to feed this powder in the TS torch, becomes very poor below about 10 µm. Nevertheless, this working direction appearing as essential, several ways were considered in order to reduce the particles size and obtain finer microstructures.

A first way consists in reducing as much as possible the size of the powder particles (e.g., down to 5 µm) by carefully selecting the powder feeder and the particle size repartition inside the powder and to implement specific spraying parameters, for example under controlled atmosphere. In that way, for example Zhang et al. [16] were able to significantly reduce the porosity of as sprayed YSZ

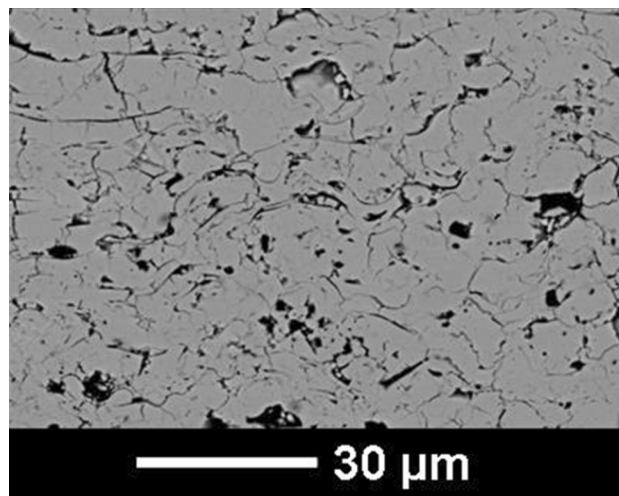


Fig. 1 Typical structure of a thermal spray ceramic layer

layers, but not to suppress it. Another way would consist in changing the medium supporting the powder from gas (usually argon) to liquid. The technique is nowadays known as suspension plasma spraying (SPS). The suspension is slurry composed of micron, submicron or even nanosized particles and a dispersant such as water or alcohol. Meanwhile, in those conditions, the high energy necessary to evaporate the liquid phase of the suspension reduces the amount of slurry, and thus of ceramic powder, which can be fed in the torch and requires a high enthalpy jet such as a plasma jet together with very specific spraying parameters.

Further ways consist in adapting the spray parameters and spray conditions, selecting the most appropriate spray gun and even applying post treatments to the deposited layers, such as laser remelting, sintering or impregnating with a solution.

Meanwhile, besides those difficulties and ways of remediation that require specific developments, owing to its high versatility in terms of materials composition and structure (porosity range) of the deposited layers, TS offers the possibility to fabricate the entire membrane-electrodes assembly (MEA) of a fuel cell, thus offering convincing potential cost reduction in view of industrial production [17, 18]. Given the typical range of melting temperature of ceramics, plasma torches are especially convenient for the application of ceramics. Solid electrolytes being ceramics of oxide type, the simple and low cost atmospheric conditions are thus generally employed. For example, Ju and Hong [19] were able to produce a complete tubular fuel cell starting from a porous TS formed 3 % YSZ tube as the support, followed with a porous LSM layer as the cathode, then a dense 8 % YSZ layer as the electrolyte and finishing with a porous Ni-8YSZ cermet as the anode using only conventional atmospheric plasma spraying (APS). The recorded performance was modest (about 3 mW/cm<sup>2</sup>), but the cell was tested at a temperature of 600 °C.

A similar work was made by Ma et al. [20] for a planar arrangement of the cell and using LSGM (La<sub>0.8</sub>Sr<sub>0.2</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3</sub>) as electrolyte material. Results were also considered as “promising” with nevertheless the same question of the specific conductivity of the electrolyte. These (and others) studies having put in evidence the main problems associated with TS fabrication, i.e., phase and interface stability, electrolyte conductivity, gas tightness and mechanical behaviour, and later experimentations tried to address those questions. Zheng et al. [21] addressed the question of the mechanical strength of the cell by using a metal support and that of the conductivity of the electrolyte layer by reducing its thickness. Meanwhile, gas tightness of the electrolyte was hardly achievable below 150 μm in thickness and the resistivity of the electrolyte remained a problem. The open circuit voltage (OCV) of the fabricated

cell was close to 0.95 V and the maximum power density (MPD) was about 100 mW/cm<sup>2</sup> at 800 °C and 0.7 V. Optimizing the spraying parameters (plasma gas composition, powder feedstock selection), Syed et al. [22] were able to improve the characteristics of previous “state of the art” YSZ electrolyte layers reaching 196 mW/cm<sup>2</sup> at 800 °C and 0.7 V. With the help of improved TS torches such as the Triplex® of Sulzer-Metco, Vassen et al. [23–25] were able to further reduce the electrolyte layer thickness to about 40 μm and obtain a power density of 500 mW/cm<sup>2</sup> at 0.7 V and 800 °C; the OCV of the cell remained close to 950 mV.

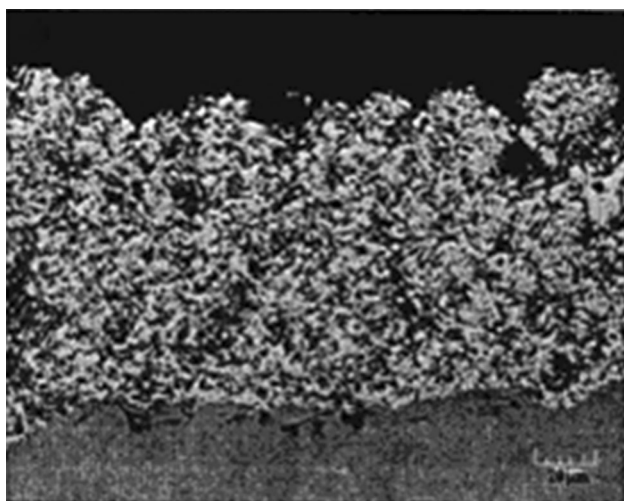
Besides improving spraying parameters, post processing of TS deposited layers was considered as an option to overcome the difficulties linked to the properties of the sprayed structures (cracks, porosity). Meanwhile, classical densification processes based on high temperature recrystallization are not suitable as they will promote interdiffusion between the layers and cracking during the cooling stages. Therefore, Zhang et al. [26] developed an original process of deposit densification using microwave sintering. YSZ layers presenting little interactions with microwaves, they introduced a dopant (BaTiO<sub>3</sub>) as electromagnetic susceptor in order to concentrate the thermal energy in the electrolyte layer. With an amount of about 5 wt% in the YSZ, the electromagnetic coupling was sufficient to perform the microwave heat treating. This treatment led to an interesting increase of about 60% in the ionic conductivity versus as-sprayed pure YSZ, which is interesting but hardly reach the situation of bulk YSZ. Li et al. [27, 28] developed an impregnation process using nitrate salt solutions of zirconium and yttrium. The gas permeability of the electrolyte layer was thus reduced by a factor of 10, but the electrical conductivity was only slightly improved and remained low (about 10 times less than bulk zirconia) given the anisotropic structure of the sprayed and impregnated layer.

Khor et al. [29] considered the use of the spark plasma sintering process in order to densify APS deposited 7 YSZ layers. In this process, an electrical discharge through the deposit associated with high pressure induced a sintering process. A microstructure transition from layered-type to granular-type was observed above 1,200 °C as well as a significant reduction in the porosity above 1,500 °C. This temperature was nevertheless probably much too high to lead to industrial application. Thus, the perception that spraying conditions had to be improved versus that of the standard APS technique in order to obtain denser and more homogeneous layers soon developed in the community.

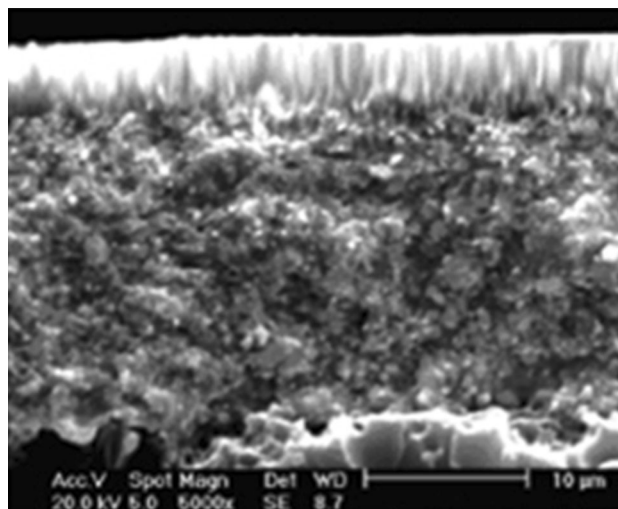
Spraying under low pressure of argon gas (LPPS or VPS techniques) is known to greatly help in obtaining very dense and recrystallized layers of metals and alloys [30]. The situation is not so clear for ceramic materials but with

the use of adapted powder grain size, thin and dense layers of ceramics were obtained by several authors, with the drawback of higher cost versus APS of course. Thus, Ma et al. [31] using low pressure environmental conditions, fine YSZ powders and he based plasmas obtained thin (about 20  $\mu\text{m}$ ) and dense (porosity below 1%) layers of electrolyte but the gas tightness and electrical conductivity were not measured; Zhang et al. [32] and Verdy et al. [33] obtained similar results. Lang et al. [34], increasing the substrate temperature under low pressure conditions, were also able to produce fairly dense and gas tight electrolyte layers in the thickness range 40–50  $\mu\text{m}$ . Corresponding cell performance was 330  $\text{mW}/\text{cm}^2$  at 900  $^\circ\text{C}$  and 0.7 V with  $\text{H}_2$ /air feeding. Considering the potential interest of using feedstock material with very fine grain size in order to limit the defect size in the deposited layers and given the difficulty to feed a plasma gun with fine grain size powders, the idea of using powder suspensions in a liquid phase was soon spread in the TS community. At the very beginning of its use, SPS results were somewhat disappointing [35–37] as the high energy loss associated with the introduction of the liquid phase in the plasma generally conducted to highly porous structures (that may have their own applications) instead of dense layers (see Fig. 2). Nevertheless, progressive understanding of the phenomena allowed making some progress with respect to the deposition of dense layers [38] (see Fig. 3).

Thus, Brousse et al. [39] prepared 10  $\mu\text{m}$  thick YSZ electrolyte layers using nanosized feedstock suspensions while Oberste Berghaus et al. [40] and Hui et al. [41] made use of adapted high velocity oxy fuel (HVOF) spraying conditions (high fuel / oxygen ratio, ethanol or ethylene glycol suspension phase, low standoff distance,...) in order to spray ceria based electrolyte layers of 20  $\mu\text{m}$

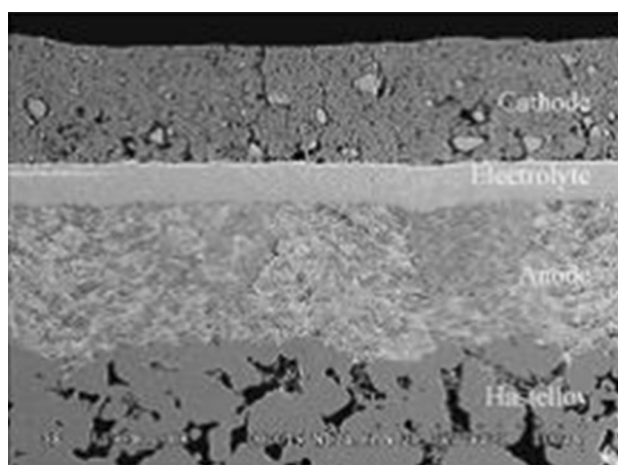


**Fig. 2** Cross section of a YSZ layer obtained by SPS after Rampon et al. [37]



**Fig. 3** Fracture of a YSZ layer obtained by SPS after Fauchais et al. [38]

average thickness (see Fig. 4). The corresponding cell performance was about 700  $\text{mW}/\text{cm}^2$  at 700  $^\circ\text{C}$  and 0.7 V. Meanwhile the authors pointed out that this performance could not be maintained after thermal cycles due to the loss of contact between the electrolyte and the electrodes arising from the mismatch of thermal expansion coefficients between the components. More recently, Xia et al. [42] studied the fabrication of SOFC using a “hybrid process” combining APS for porous electrode deposition and SPS for dense electrolyte deposition thanks to the smallest grain size that can be used in SPS process. Using this approach, a high densification, a low thickness and a homogeneous material composition was achieved.



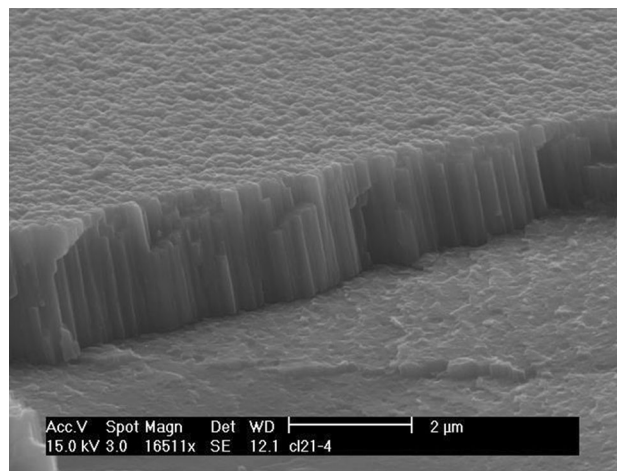
**Fig. 4** Cross section of a HVOF sprayed cell composed of a porous metallic substrate, a samarium doped ceria (Ni-SDC) anode and a dense SDC electrolyte. The cathode composed of a mixture of samarium strontium cobalt oxide (SSCO) and SDC was screen printed on top of the previous arrangement, after Hui et al. [41]



So it can be observed that significant progress has been regularly made during the past 10 years with the TS technology and therefore it can be imagined that further progress is certainly possible in the near future concerning the deposition of high performance SOFC electrolyte layers between 10  $\mu\text{m}$  and 20  $\mu\text{m}$ . Meanwhile, the layer thickness being of primary importance and owing to the deposition principles, people developing the PVD techniques are now considering the possibility to produce electrolyte layers in the thickness range below 10  $\mu\text{m}$  (again for high power SOFCs) as this range of thickness is already reached for small size devices [63].

#### 4 PVD

PVD techniques have been much less used than TS to produce SOFC electrolyte layers, probably because the deposition rate is at least 100 times smaller than that of the latter, which is a strong handicap in view of mass production. Nevertheless a number of studies have been performed recently, most dealing with the problem of controlling the composition and the structure of the deposits. Vapour phase deposition is a technique by which a material is evaporated, generally in a vacuum chamber, and subsequently condensed on a substrate where it forms a layer. The vapour phase may be simply obtained by heating the material or sputtering it with ions such as argon ions. A superposition of an electric field and/or a magnetic field allows to increase the energy and the density of the atoms and thus to modify the structure and the deposition rate of the film. The structure of the deposited layer mainly depends on the energy of the incoming species which is strongly dependant on the chamber pressure and substrate temperature [43] and also on the orientation of the substrate versus the flux. A typical structure of a magnetron sputtered ceramic film is shown in Fig. 5. This structure is generally composed of columnar grains oriented perpendicularly to the substrate, but it may be modified depending on the deposition parameters [43]. When the deposited material is a compound, such as ceramic, an important feature of the deposit is its stoichiometry. While this characteristic may be more or less easily maintained using ceramics as precursor material, this option is severely hindered by the low sputtering rate of dielectrics which is generally performed using RF sources. Therefore, sputtering a metallic target under reactive conditions, i.e., introducing a reactive gas (e.g., oxygen in the case of an oxide ceramic) in the deposition chamber is generally a preferred route as the deposition rate will be roughly increased by a factor of 10. Meanwhile the process in that case is not easy to control as the stoichiometry of the deposit will depend on the oxygen partial pressure and the sputtering rate will

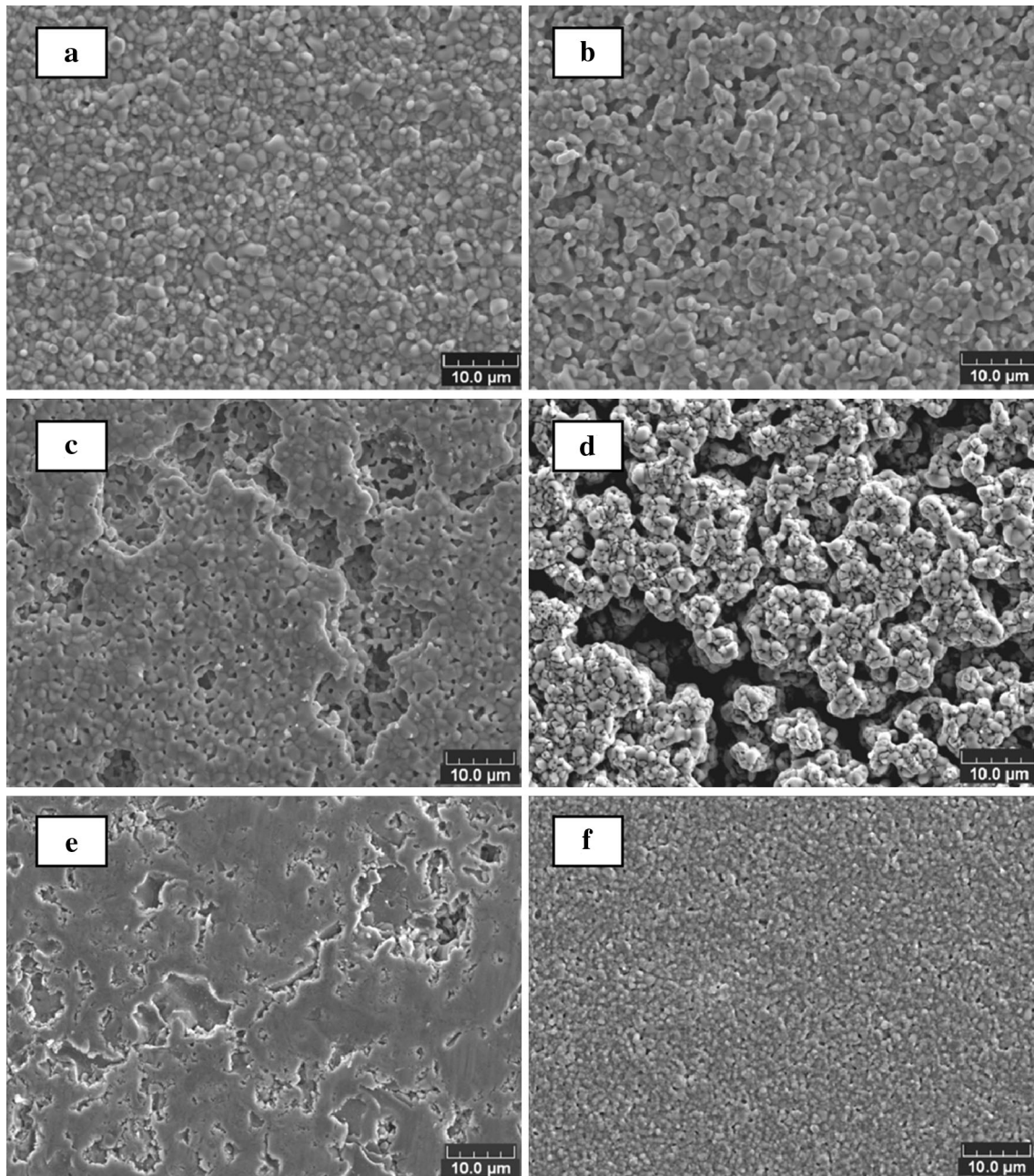


**Fig. 5** Typical structure of a PVD ceramic layer

vary according to the degree of reactivity of the target material with oxygen.

Most of the early works on SOFC dealing with PVD deposited layers were concerned by the electrical resistance of the electrode/electrolyte interface [44, 45] or the composition and structure of the film, as said before, and then little attention was paid to the problem of laying down thin, compact and gas tight films on porous substrates such as those shown in Fig. 6 which displays the surface morphology of several anode materials originating from different laboratories or companies. The porosity of the electrodes being required in solid fuel cells for the delivery of the reactants, and the option of building the electrolyte first being hardly conceivable for thin films in the micron thickness range, the challenge of depositing a thin electrolyte layer on a porous substrate appears as a key point of the process. Those observations were also reported by Nedelec et al. [46] when trying to lay down thin (1  $\mu\text{m}$ ) PVD layer on substrates having pores about 3  $\mu\text{m}$  in diameter. In fact, as indicated before, most of PVD layers are generally deposited on polished substrates like glass or silicon [47–50] and thus results are hardly relevant for the production of MEA.

A number of works were also dealing with more sophisticated compounds than YSZ, such as gadolinia doped ceria (GDC) or lanthanum molybdenum oxide (LaMO $x$ ) [51, 52]. But as mentioned before the practical application of those high conductivity compounds is severely hindered by their poor stability. Considering the electrode/electrolyte situation in the cell arrangement using Pt as electrode material, Nakagawa et al. [53] elaborated thin YSZ electrolyte films using magnetron sputtering of a pressed mixture of zirconia and yttria powders. As oxygen deficiency was observed after sputtering under argon atmosphere, they subsequently implemented air baking of their specimens for 1 h at 1,170 K. Unfortunately, the

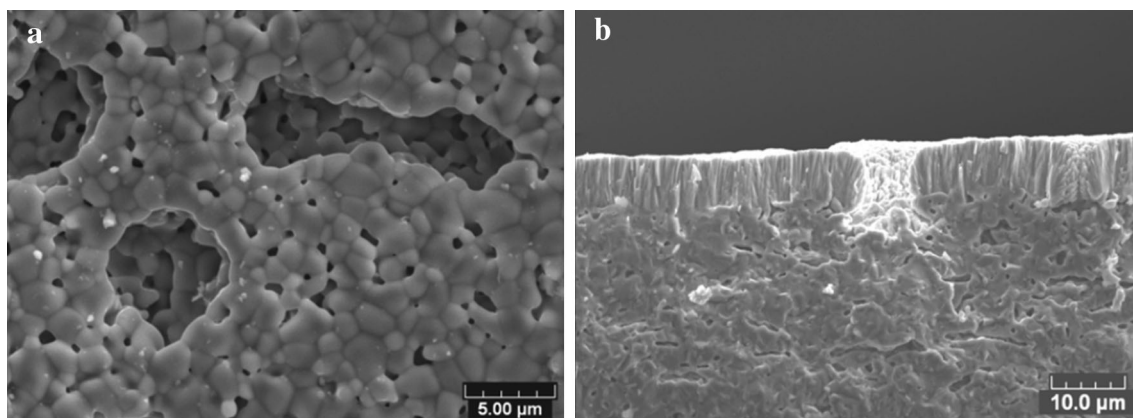


**Fig. 6** Micrographs showing the surface state of several anode materials (Ni-YSZ cermet) which could be used as supports for the electrolyte layer, **a** CeramTec 5% porosity, **b** CeramTec 30% porosity, **c** InDec, **d** Julich, **e** LERMPS, **f** SOFC power

performance of the cell fed with air and hydrogen was only about  $7 \text{ mW/cm}^2$  at  $0.7 \text{ V}$  and  $740 \text{ }^\circ\text{C}$ . The YSZ electrolyte thickness being about  $12 \text{ }\mu\text{m}$ , the performance limitations were considered to be due to the poor efficiency of the contact zones between the electrodes and the electrolyte, the latter being quite homogeneous. Tsai and Barnett [54] demonstrated later that dense YSZ films of thickness lower than  $5 \text{ }\mu\text{m}$  could be produced via reactive sputtering deposition on porous substrates such as LSM, providing the substrate was prepared in such a way that porosity was fine

(pore size below  $0.5 \text{ }\mu\text{m}$ ) and a bias voltage was applied on the substrate. Under those conditions, the number of defects was reduced and the recorded OCV of the corresponding cell was close to the theoretical value. Srivastava et al. [55] also prepared thin ( $5\text{--}16 \text{ }\mu\text{m}$ ) YSZ films on porous (32%) NiO/YSZ substrates by DC magnetron sputtering of a composite Zr-Y target under a reactive atmosphere. The authors did not make use of substrate bias but they preheated the substrate between  $300 \text{ }^\circ\text{C}$  and  $500 \text{ }^\circ\text{C}$  prior to the deposition of the YSZ film. Only a



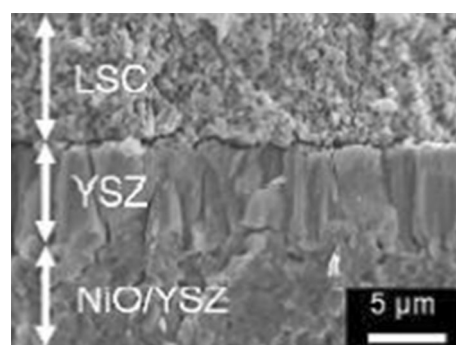


**Fig. 7** SEM micrographs of large surface defects in the Ni/YSZ cermet substrate **a** and the corresponding through thickness defect in the YSZ sputter deposited electrolyte layer **b**, after Coddet et al. [56]

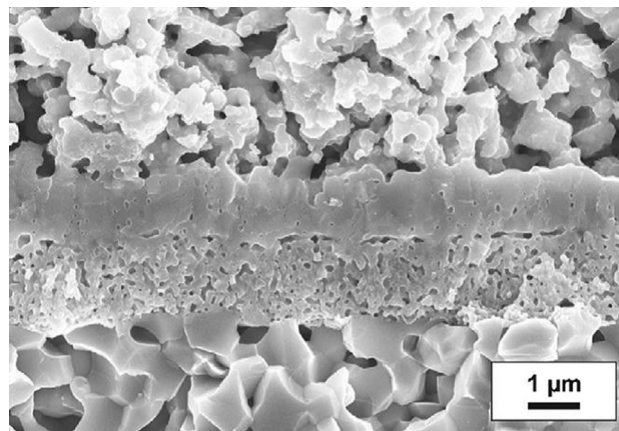
narrow range of deposition conditions was found to be suitable. In order to reach gas tightness and prevent film spalling, they had to use a multiple steps deposition process, performing heat treating (in air at 1,200 °C) for each deposited YSZ sub-layers before laying down a further layer. Using a screen printed LSM cathode deposited on the YSZ, the MEA was electrochemically tested with hydrogen and air and the performance of the cell was established at 330 mW/cm<sup>2</sup> at 750 °C and 0.7 V, with an OCV established at 1,100 mV. In fact, it must also be pointed out that if the preparation mode (powder sintering) of the Ni-YSZ cermet constituting the anode yielded to a porosity of 32 % with a bulk pore size ranging from 0.5 μm to 10 μm, the surface porosity of the samples was much smaller due to enhanced sintering at the surface.

More recently, Coddet et al. [56, 57] using a closed loop control system based on optical emission spectroscopy were able to achieve, with reasonably robust and fast conditions, dense YSZ thin films on porous Ni/YSZ anode cermets using magnetron sputtering of Zr and Y or ZrY targets in a reactive mode [56, 58]. The size and depth of the surface pores of the substrate had nevertheless to be selected in order to be adapted to the process and thus avoiding through thickness defects (see Fig. 7). Deposition conditions were also selected in such a way that the as deposited YSZ film should be slightly oxygen deficient while further oxidation treatment in air was bringing it to a fully oxidized state with acceptable compressive residual stresses. Performance of the cell fed with air and hydrogen was about 560 mW/cm<sup>2</sup> at 0.7 V and 800 °C [59]. A SEM micrograph of the corresponding cell is presented in Fig. 8.

Nedelec et al. [46] demonstrated that an improvement of the layer morphology and of gas-tightness could be obtained with increasing bias power applied to the substrate. This allowed the change of the layer growth morphology from columnar to more isotropic structure



**Fig. 8** SEM micrographs of a cell elaborated with an electrolyte deposited by magnetron sputtering, after Coddet et al. [59]



**Fig. 9** SEM polished cross-section of a  $\approx 1$  μm thick PVD deposited electrolyte in a cell (after electrochemical performance testing), after Nedelec et al. [46]

and prevented crack formation (see Fig. 9). Thus, the decrease in the area specific resistance led to an increase of the performances (about 600 mW/cm<sup>2</sup> at 0.7 V and 650 °C).

It can also be noticed that PVD can be used for the manufacturing of interlayers (also called “functional” layers) presenting specific properties (e.g., avoiding interdiffusion) and structure (e.g., adequate porosity, enhancement of the number of triple phase boundaries). One advantage of PVD and more generally the use of low deposition temperature processes is to minimize the risk of elements interdiffusion between adjacent layers. As an example, Han et al. [60] deposited a  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$  layer between a 8 YSZ electrolyte layer and a  $\text{La}_{0.58}\text{Sr}_{0.40}\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3-\delta}$  cathode layer in order to prevent Sr-diffusion during the manufacturing and operation of the SOFC cell. Recently, based on the reduction of the electrolyte thickness, the use of appropriate interlayers and a low temperature deposition avoiding interdiffusion of elements, multilayers cells were developed exhibiting excellent performances such as  $1,100 \text{ mW/cm}^2$  at 0.7 V and 650 °C [60–62].

## 5 Conclusions

Quite interesting progresses were made during the past few years regarding TS and PVD deposition techniques owing to a better understanding of the build up mechanisms of thin oxide ceramic layers. Operating temperature of the SOFC was decreased thanks to thinner electrolyte layers, better ionic conductivity and lower contact resistances. Meanwhile, performance results presented in the literatures must be considered very carefully due to the variety of the measurement conditions. In fact, short term recorded data such as MPD and OCV are not especially significant to compare cells performance. A more systematic use of more practical data such as the energy density at a given temperature and voltage (for example 0.7 V) would be very desirable. During the last decade, many people oriented have their work towards the development of “exotic” electrolyte compositions and thus less attention has been paid to the improvement of well-established materials such as YSZ for the electrolyte for which there are certainly still ways of improvements in terms of quality, reproducibility, and economical processing. TS and PVD techniques are certainly not at the end of their capability on that way.

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