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Tape Casting Ceramics for high temperature Fuel Cell applications

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1. Introduction

1.1. General

The objective of this book chapter is to detail how to apply an a priori easy to implement shaping technique to fabricate high temperature fuel cell elements. High temperature fuel cells (SOFC for Solid Oxide Fuel Cell, PCFC for Proton Ceramic Fuel Cell) are sophisticated objects, made of thin active elements differing in composition and microstructure ($\approx 50\text{-}300\ \mu\text{m}$ porous cathode, $10\ \text{to}\ 50\ \mu\text{m}$ dense electrolyte, $50\text{-}300\ \mu\text{m}$ porous anode, typically) that are operated at high temperature (from $500\ \text{°C}$ to $1000\ \text{°C}$, typically) and that are supposed to last some 40000 hrs under oxidizing atmosphere on the cathode side and reducing atmosphere on the anode side. The fabrication costs of high temperature fuel cells remains the major brake against their rapid development. Tape-casting is a supposedly low cost and simple shaping process, but it appears to become quickly complicated to implement if it aims at producing a thin tri-layer ready for co-sintering as it can be the case in high temperature fuel cells. The operability of tape-casting requires that one understands clearly each step of the process, from the slurry formulation to the final sintering treatment via the drying step. The present text offers a discussion about tape-casting and co-sintering of the bi- or tri-layers components of SOFCs and PCFCs, and gives some indications on how to circumvent the difficulties in certain cases. It raises several important issues and problems regarding aqueous and organic tape-casting. It shows that each step of the process is important, but that the formulation of the slurry is crucial for the final product. It gives also evidence that this process requires to be backed by modelling and computer simulation to take into account all the mechanisms that lead to instabilities and residual deformation. This book chapter is illustrated by concrete examples and micrographs from the fabrication of YSZ based SOFC and BCY10 based PCFC, but also from the first attempts to realize a new type of high temperature fuel cell (IDEAL-Cell) based on an innovative new concept under intensive research in a European consortium today; they show that in some cases tape-casting and co-sintering are impracticable, and that a sequence of processes is highly preferable than a single process.

1.2. High Temperature Fuel Cells context

Solid Oxide Fuel Cells are promising power generating systems which are currently based on anionic solid conductors (SOFC), mostly Yttria-Stabilized Zirconia (YSZ), or more recently on protonic conductors (PCFC) in which the electrolyte may be an yttrium doped barium cerate (BCY) or zirconate (BZY) (see Fig. 1 and 2). The operating temperature of YSZ-based SOFC is usually high ($> 900\text{ }^{\circ}\text{C}$) in order to reach the highest anionic conduction performance. This presents significant advantages (chemical stability with CO and CO_2 , direct CH_4 feeding, etc...), but also severe pitfalls (thermomechanical failure of components, sophisticated glass seals, chemical instabilities during ageing and cycling...). These difficulties can be significantly diminished if the operating temperature is reduced to $600\text{ }^{\circ}\text{C}$ - $700\text{ }^{\circ}\text{C}$; but then the loss of conductivity associated with the temperature drop must be compensated either by changing the electrolyte material (*i.e.* shifting to Ceria) or by drastically diminishing the electrolyte thickness.

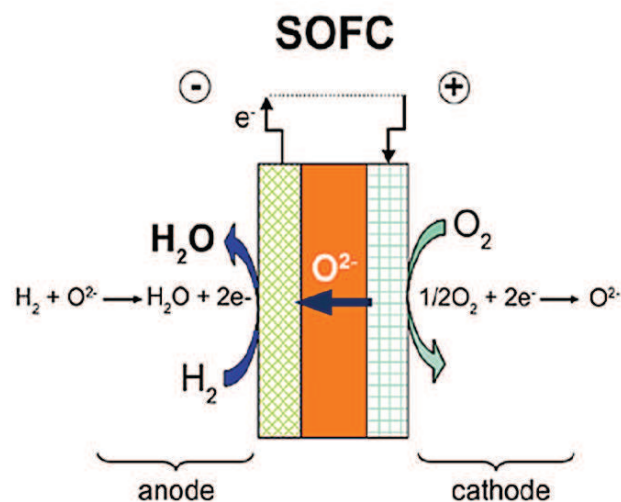


Fig. 1. SOFC, water at the anode side

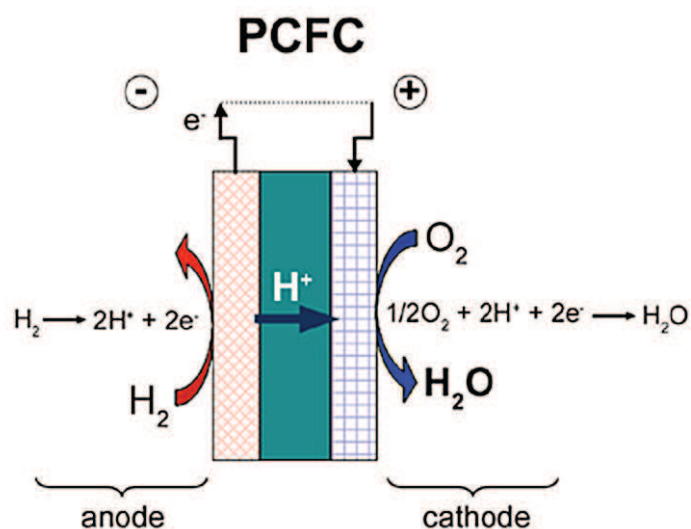


Fig. 2. PCFC, water at the cathode side

PCFCs are quite credible alternatives, though at a much less mature state of development than SOFC. Among all the perovskite based proton conductors, 10% Yttria-substituted

Barium cerate (BCY10) is widely studied for its high level of protonic conduction below 700 °C under hydrogen-and/or water-containing atmospheres (10^{-2} S cm^{-1} at 600 °C under wet hydrogen). But this class of materials displays some particularities (high basicity, high sensitivity to water and CO_2 , high refractivity, chemical decomposition at high temperature, residual oxygen conduction under certain conditions...), which make them requiring still a certain amount of basic research prior to development. An innovative design is under scrutiny for a couple of years now (IDEAL-Cell); it consists of a mixed conducting cell that will potentially eliminate all the problems associated with the presence of water at electrodes in both SOFCs and PCFCs since the water is formed and evacuated from a porous central membrane made of a composite of the two types of electrolytes (Fig.3)(see www.ideal-cell-eu; Thorel et al, 2009a; Thorel et al, 2009b).

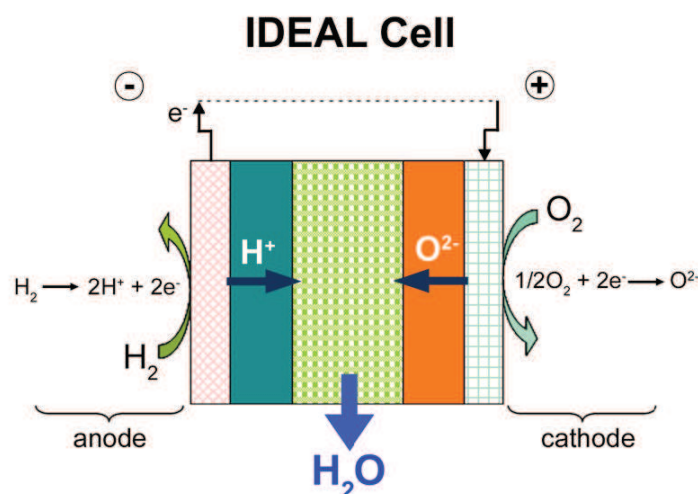


Fig. 3. IDEAL-Cell concept, water production in the central compartment

1.3. Designs and Fabrication Processes

The general geometries for these high temperature cells -at least SOFCs and PCFCs, IDEAL-Cell being just at the proof of the concept step- are either planar or tubular, industrials giving their own twist between these two basic designs. Though less tested on the long term, planar designs provide a higher current density than tubular designs, between 0.50 and 1.5 W cm^{-2} . The major brake to the development of high temperature fuel cells is the cost of fabrication compared to the market requirements. Whatever the geometry, a single cell is a complex quasi-2D multilayered structure made of different sophisticated materials having different microstructures and functions. If one focuses on the planar geometry, many processing routes can be envisioned, but the community considers only a limited number of low cost shaping processes. They can be divided into 2 classes, i/ those that require the use of a slurry (tape-casting, screen-printing, slip-coating, dip-coating...), and ii/ those in which the powder is projected on a target (essentially plasma spraying related deposition processes). Other excellent processes (PVD-CVD, SPS, hot-pressing...) are a priori too expensive and difficult to scale-up, and therefore not competitive enough to meet with the market constraints (*i.e.* US SECA program cost target = \$400/kW by 2010). Plasma-spraying, tape-casting and screen-printing have given first-rate results for fabrication of SOFCs [Hui et al, 2007; Syed et al, 2006; Grosjean, 2004; Bitterlich et al, 2001; Xia et al, 2001]. Surprisingly, very few studies have been carried out so far on shaping PCFC via these processes (Costa et

al, 2009; Hafsaoui, 2009; Costa, 2009), which are all presently considered for shaping IDEAL-Cell (Presto et al, 2009).

Ideally, a low-cost process that allows co-sintering the multilayer would be very profitable in terms of fast development of SOFCs or PCFCs; but this is an extremely difficult problem that aims at obtaining flat well bonded layers with appropriate densities and fine-tuned microstructures, with no appearance of cracks, secondary phases, chemical reactivity, unwanted allotropic transformations. Apart from processes derived from the plasma deposition and if we focus on the more traditional ceramic processes, the previous characteristics are all being governed ultimately only by three common parameters: sintering temperature, duration of the treatment and atmosphere. Obviously, this very limited number of levers that we can act on for co-sintering can only trigger a differentiated evolution of the layers only if the green layers have the potential to allow for it, that is to say exhibit an appropriate geometry, composition, grain size distribution, initial density... The green layers characteristics are in turn completely determined by the slurry composition and powders morphology, the way the layers are superimposed and bonded, and how the multilayer is being dried prior to sintering. In the present paper, that gathers results from different projects (Grosjean, 2004; Costa et al, 2009; Hafsaoui, 2009; Costa, 2009), we will focus on the problems encountered when one fabricates SOFC and PCFC by tape-casting and co-sintering, and will detail some of the ideas suggested above.

2. Shaping by tape-casting

2.1. General considerations on tape-casting

Tape-casting is a low cost process particularly well-suited for the fabrication of thin (10 μm up to 500 μm) flat components for high temperature fuel cell. It allows producing a wide variety of controlled morphologies, from highly porous to fully dense microstructures, such as electrodes and electrolytes. Green layers can be easily superimposed if one wants to co-sinter the multilayer in a one-step operation. As seen in Fig. 4, the whole process gathers consecutive steps: the first one and probably the most important is the fabrication of the slurry with the powder under consideration, which is previously formulated, calcined and eventually sieved to reach appropriate phase content, grain size distribution and morphology.

Organic and/or inorganic additives, which role will be described below, are added to the powder to form the slurry. The slurry is then mixed and grinded mostly by ball-milling to ensure homogenization and destruction of agglomerates. Then the solution is de-aired under primary vacuum depending on which level of porosity/density is desired at the end of the process. The slurry is then ready for the casting of a green tape, which thickness is governed by the height of the Doctor blade above the substrate (Fig. 5 and Fig. 6). The ratio between the green and the sintered sample thicknesses depends on the properties of the slurry and on the degree of freedom of the system when the layers shrink during drying and during sintering, which in turn depends on numerous intrinsic parameters (*i.e.* those taken into account in a dilatometry curve, such as powder nature, size, composition and formulation of the slurry, temperature and duration of sintering...), but also on extrinsic parameters linked to the nature of the substrates for drying or sintering, that may lead to friction and wear inhibiting radial shrinkage and increasing then the level of vertical/longitudinal shrinkage.

This may even be more effective if a light weight is deposited on top of the samples to maintain its flatness. The different wet layers can then be cast on top of the others via dedicated technical systems (*i.e.* series of Mylar masks) if the solvent is organic; if the solvent is water, then the layers must go through a gel-forming step prior to superimposition since otherwise they do not exhibit any mechanical strength. Technical adjustments can be carried out between these two solutions, but it is important to note that a good final bonding between two layers requires that at least one layer is wet. Drying single layers or multilayers is also a prime importance step. Any geometric deformation or defect occurring during the drying process will only worsen during sintering. It is therefore essential that the flatness be maintained, depending on how isotropic the mechanism of humidity withdrawal is, above, below and along the radius of the sample. If one uses a dense substrate, then humidity cannot escape from the bottom and the dried sample is usually warped with strong deformation in the $z+$ direction, along with edge sinusoidal deformation. Sandwiching the sample between two dense substrates does not usually help and ends up with extensive cracking. We have had excellent results when sandwiching the layers or multilayers between two light honeycomb Mullite substrates left at 70 °C (Fig. 7).

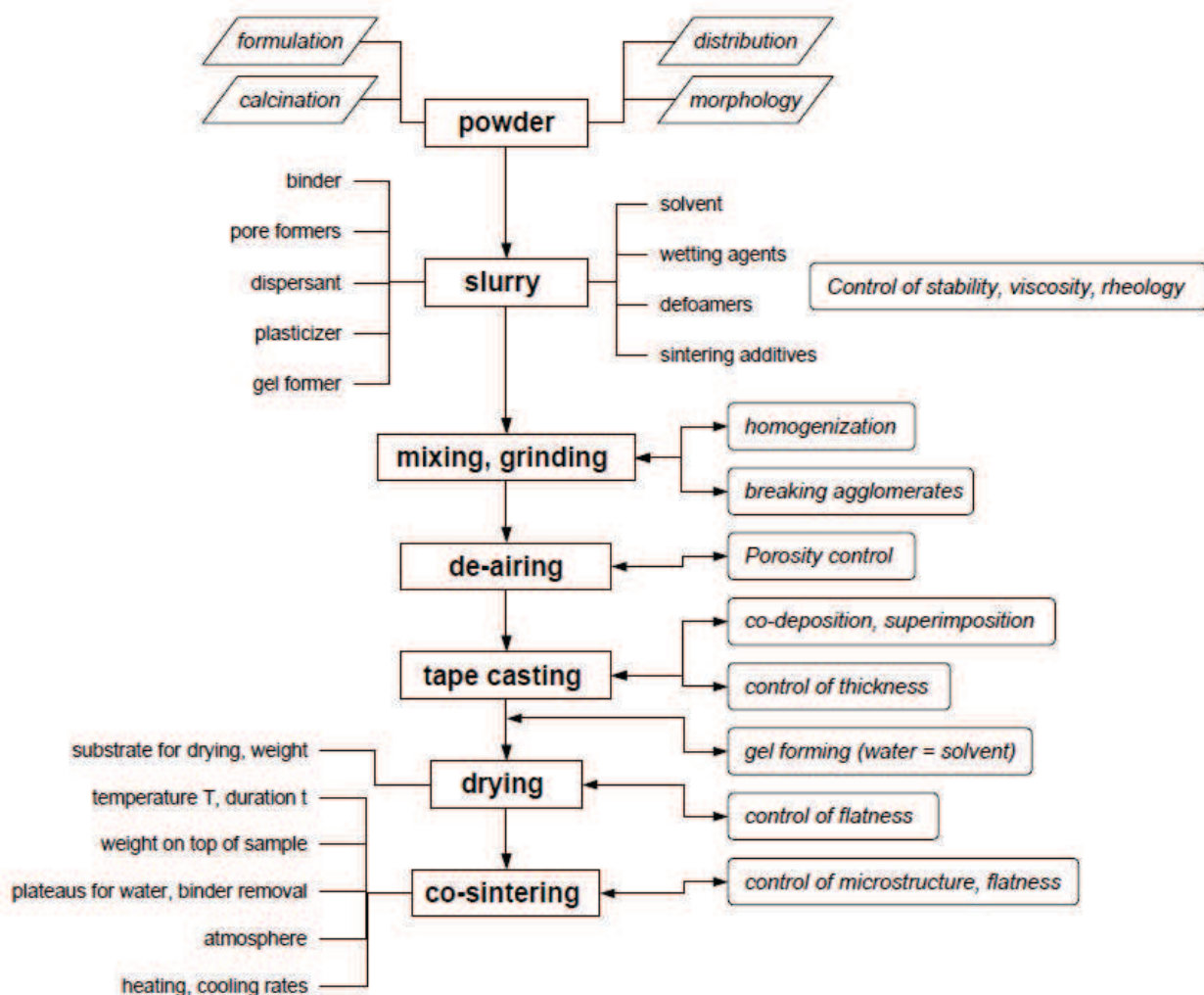


Fig. 4. Flowchart for organic or aqueous tape-casting and co-sintering of multilayers

We have shown thus that the drying mechanism was related to the evacuation of liquid water facilitated by capillary forces acting across the sample, thanks to the porous honeycomb supports, which in addition were efficient to maintain the flatness of the sample (Grosjean, 2004; Costa et al, 2009).

Obviously, the sintering step is the key-moment of the whole process. One should not use more time and temperature than what is needed; therefore the level of the sintering temperature and duration will be as little as possible.

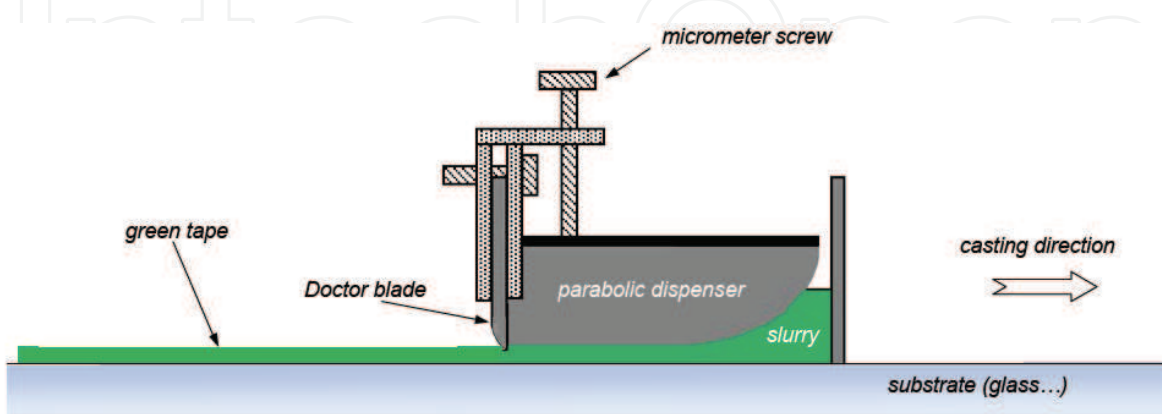


Fig. 5. Schematic of a laboratory tape-casting set-up

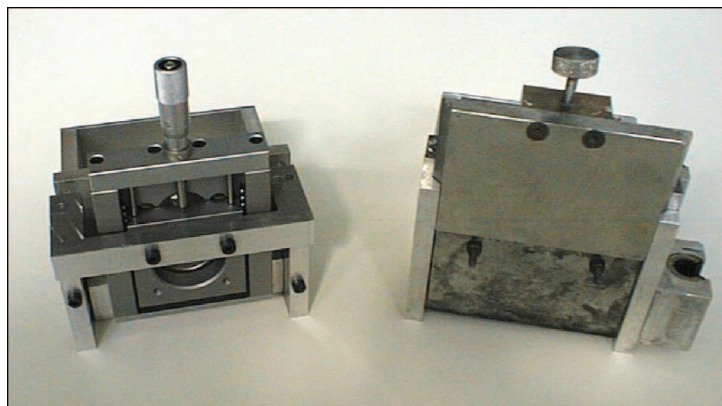


Fig. 6. Tape-casting experimental set-up

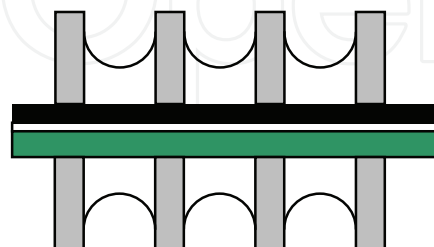
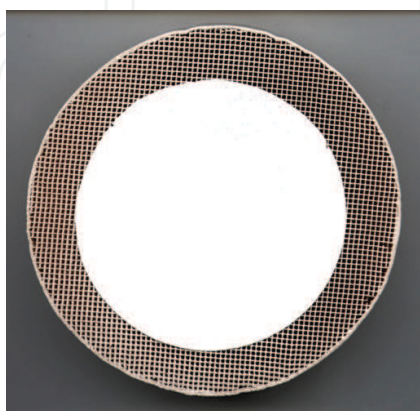


Fig. 7. Drying of a YSZ layer sandwiched between two Mullite honeycomb substrates (left); detail of the capillary mechanism acting across a SOFC trilayer during drying between 2 honeycomb substrates

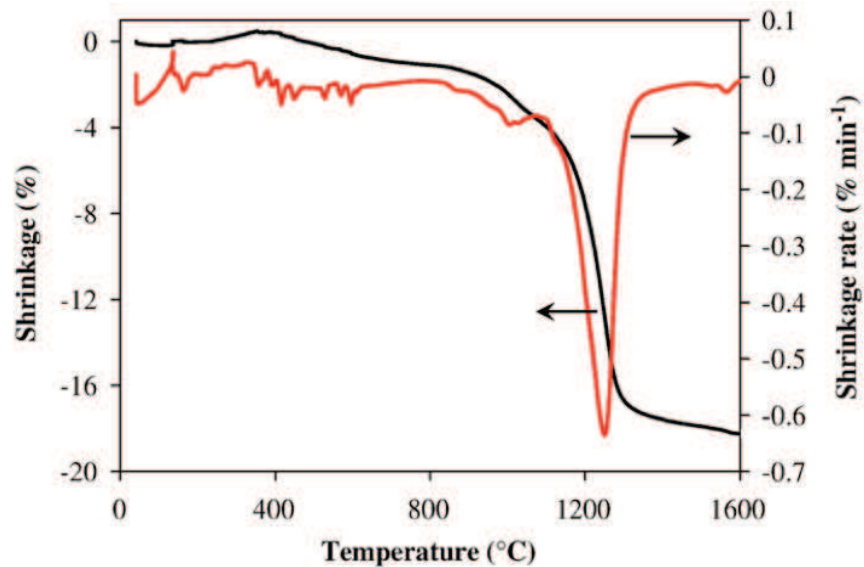


Fig. 8. Shrinkage curve for BCY10; left: shrinkage (%), right: shrinkage rate (% mm⁻¹) (from Bassano et al, 2009)

The sintering temperature is usually chosen as to correspond to the temperature where the sintering rate is maximum (*i.e.* 1250 °C for BCY10 in Fig. 8 from Bassano et al, 2009); in that case a density higher than 95% of the theoretical density is attained rapidly with very limited grain coarsening if the slurry has the characteristics for a fully dense final material. This may be adapted if one wants to obtain a porous final material or in the case of co-sintering of multilayers. The choice of the support is of uttermost importance since it must obviously not react with the sample and must not present any roughness that could generate unwanted friction and interference with the radial shrinkage. Ideally the support should be made with the same material as the layer in contact with it. Sometimes a powder bed is used as a buffer for reactivity, but in that case the powder bed has to be thin and very flat.

2.2. Details on the slurry formulation

For a given powder or mixture of powders the sintering behaviour of green tapes, and hence their final microstructure, depends on the arrangement, dispersion and homogeneity of the starting ceramic particles in the slurry (Moreno, 1992a); therefore, the slurry formulation is a crucial step for tape-casting, as it is also for related processes such as screen-printing, spin or dip-coating. Roughly, a good slurry is the one in which the ceramic grains are electrostatically interacting so that the particles are the farthest away from each other, that no agglomerates are formed, that gravity is negligible, hence no sedimentation occurs, and so that the viscosity is low enough to allow for an easy casting, and high enough for the green tape to have a sufficient creep resistance to maintain its geometry. As a rule of thumb, and respecting the indications given above, the highest possible the ratio solid/liquid, the highest the density of the green tape, hence the highest the density of the sintered tape.

Generally, the slurry is composed of a mixture of numerous organic compounds (binder, dispersant, plasticizer (Moreno, 1992b), solvent if organic tape-casting, and possibly wetting agents, defoamers, pore formers if needed) and inorganic compounds (ceramic powder to be

shaped, sintering additives, water if aqueous tape-casting). All the organic components remain in the green tape after drying. Since they are removed when heated at elevated temperature in air (between 300 °C and 700 °C, from polymers to graphite), they give rise to pores, which cannot -or must not- always be eliminated during the sintering treatment. Consequently, the ratio of the amount of powder to the organic compounds, and hence the final formulation of the slurry, must be fine-tuned in order to tailor the final microstructure and density. Concerning water based tape-casting, the slurry is gelled after casting and the water is removed during drying; the gel is decomposed at 350 °C at the onset of the thermal treatment giving place to porosity. Here again the ratio between the solid phase and the liquid in the slurry will tailor the level of porosity, in addition to pore formers. In both cases, organic or aqueous tape-casting, the ratio of the solid phase to the liquid/or organic phases will lead to the control of a 1-2 μm size interconnected porosity, which can be extremely useful for increasing the quantity of triple phase boundaries. Amongst the slurry characteristics, the stability is of utmost importance. Polarization interactions must take place at the solid-liquid interface, interactions whose intensity governs the slurry stability (Moreno, 1992). Consequently, the value of the dielectric constant of the liquid determines the slurry stability, and hence the choice of solvent, which in turn determines the choice of all the other additives. The other forces acting on the particles in the slurry are gravity, which depends on the particles mass (and indirectly size), and the attractive Van der Waals interactions, which promote flocculation and act against the stability of the slurry. On the other hand, thermal agitation, electrostatic and steric repulsive forces promote the dispersion of the particles and therefore increase the stability of the slurry. The role of the dispersant agent is precisely to enhance the intensity of these dispersive forces. The second important slurry characteristic is the viscosity, which determines the operability of the process to cast green tapes. The slurry viscosity varies as a function of the amount of solvent per unit volume; the solvent quantity needs to be precisely adjusted to allow for a good dispersion of the powder as well as for an efficient dissolution of the binder.

2.3. Co-sintering

- co-sintering parameters

To fabricate such sophisticated multilayered objects -SOFCs, PCFCs or IDEAL-Cells- one must have in view that the first order outcome parameter is the function of the object, and the second order outcome parameter is its long-term thermomechanical behaviour necessary to accomplish this function. Therefore efforts have to be put first on reaching the highest possible level of electrochemical properties, and once it is reached one must work on the optimization of the mechanical properties. This is a general frame that might be amended when interests converge, *i.e.* quality of the bonding at interfaces, cracking...

Obviously, during co-sintering all the layers will have to face the same treatment characterized by a given sintering temperature, duration and specific atmosphere. To a certain extent there is interchangeability between time and temperature of co-sintering through the Fick's laws and temperature dependant diffusion coefficients, provided that no unexpected thermo-activated mechanism occurs (phase change, precipitation...). This means that the common temperature is necessarily a compromise between the highest and the lowest sintering temperature of the different layers taken separately, which compromise can be smoothed to a certain extent by playing on the sintering time (*i.e.* sintering the multilayer at a temperature intermediate between the lowest and the highest sintering temperature, but for a longer time than necessary for the sintering of the less refractory layer). For a standard composition of YSZ based SOFCs and BCY

based PCFCs the usually lowest refractory layers (anode and cathode, *i.e.* respectively NiO/YSZ and NiO/BCY, lanthanum-strontium manganites and lanthanum-strontium-iron cobaltites) are also those which must be highly porous; since they will be co-sintered at a temperature higher than their normal sintering temperature, and for a longer time than necessary (so that the electrolyte can reach full density), then the slurry formulation for electrodes must be thought for correspondingly (higher Liquid/Solid ratio, addition of pore formers...) to inhibit any tendency for over densification.

The thermal treatment may also present second order parameters, such as heating and cooling rates, plateaus...; heating ramps and cooling ramps are not equivalent since at the onset of the sintering the materials are just shaped and cast powders, with no capability to transfer any elastic stress within the ceramic, whereas at the end of the sintering the material is a rigid body highly sensitive to elastic stress originating from the differential mismatch of thermal expansion coefficients between layers. The role of heating ramps and plateaus at the onset of the sintering has more to do respectively with the plastic deformation of the green layers, due to a differential behaviour with temperature, and with the complete combustion of the organic slurry compounds. It is highly important that the combustion occurs gently and completely at the lowest possible temperature so that the evacuation of gas is rendered easy via the still widely open porosity that the combustion has just created. Any increase of gas pressure inside the layers is obviously highly detrimental for the sample integrity (deformation, stresses, cracking...). The length of all the plateaus is determined by thermal analysis so that the corresponding organic compounds can totally disappear.

In most cases co-sintering necessitates reaching a certain level of compromise that can be adjusted by playing on the slurry composition and geometry of green layers (Bitterlich et al, 2001; Costa et al, 2009; Hafsaoui, 2009; Costa, 2009; Yoon et al, 2007) on the basis of the modelling of polarization mechanisms as a function of microstructural parameters (Yoon et al, 2007; Ou et al, 2009). In some cases, co-sintering appears highly impracticable, such as in SOFCs between YSZ and LSM when co-sintering above 1150 °C leads to resistive pyrochlore phases (Grosjean et al, 2006), and in PCFCs between BCY10 and NiO since we showed that there is a significant diffusion of Ni in the electrolyte material (Costa, 2009). When such difficulties arise, one must consider changing the materials or implementing a sequence of processes and consecutive sintering treatments starting from the fabrication of the layer having the highest sintering temperature and finishing with the one having the lowest (Fontaine et al, 2009). As an example, screen-printing or plasma-spraying can easily be performed on top of tape cast layers. This may be at the expenses of cost, but in that case there are less compromises to carry out and probably higher functional properties can be achieved.

- differential sintering kinetic

Deformation during sintering is composed of four terms: elastic deformation, thermal deformation, visco-plastic deformation and shrinkage due to the densification. The latter is by far the largest contribution to the overall deformation; its driving force is the reduction of surface energy and curvatures, hence the disappearance of the porosity. Different materials and/or different slurry formulations lead to strong differences in the shrinkage kinetic. Co-sintering bi-layers is extremely difficult since there is almost no way to compensate for this shrinkage kinetic differential; this is a general rule for an even number of layers. An odd number of layers is much more favourable since the deformation on one side (*i.e.* due to the bi-layer anode/electrolyte) can be compensated by the deformation on the other side (*i.e.* by the cathode) by playing on the thickness, and to a certain extent on the slurry composition (*i.e.* pore formers amount).

Obviously, one must seek a situation where deformations at both electrodes put the electrolyte layer under compression, as seen in Fig. 9.

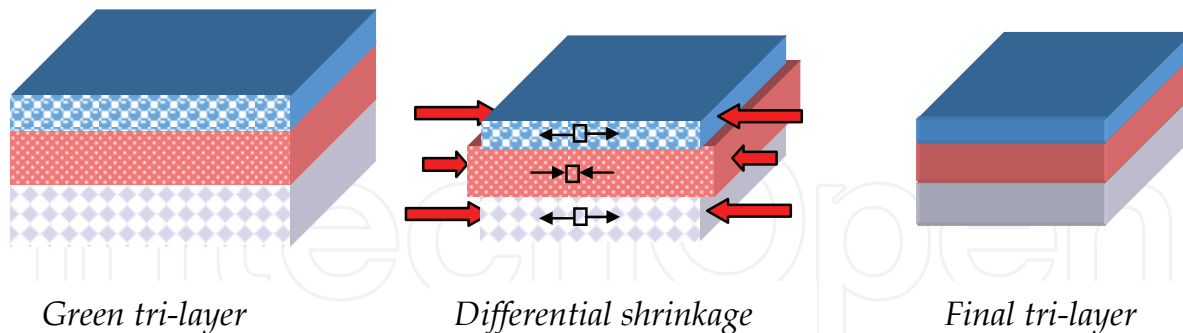


Fig. 9. Schematic of the compensation of the deformation during sintering across a tri-layer

The compensation of the deformation by the third layer may be very difficult to evaluate since it results from several mechanisms acting at different steps of the sintering. Useful information can be drawn from the observation of the final deformation of bilayers having different thicknesses, but much more efficient is the modelling of the deformation kinetic by a finite elements approach; when followed carefully, this route can reveal phenomena that occur in the furnace during the sintering, which are by essence extremely difficult to detect.

Thus, we have quantitatively detected a strong deformation peak very early at the sintering temperature originating in the differential shrinkage kinetic between a YBC10 PCFC electrolyte layer and a YBC10 + NiO PCFC anode layer; in that case, the sintering rate of the electrolyte was higher than that of the anode, whose deformation caught up little by little during the remaining time. We have also given evidence for a scale effect, the larger the diameter of the bi-layer the larger the final deformation (Costa et al, 2009). The deformation transforms into stresses if the multilayer is topped by a substrate, which aims at maintaining it flat. The weight of this substrate must be carefully tuned for allowing only planar deformation to occur, that is to say large enough to block the vertical deformation, but light enough to allow for a radial deformation. If this support is too light or too heavy, the final object will be either warped or cracked.

But nothing is free of charge regarding sintering ceramics; if one wants to identify and model quantitatively the pertinent mechanisms taking place during sintering, one must feed the model with microstructural information related to these mechanisms; this means that either we are able to gather microstructural observations during sintering -which is extremely difficult considering the high sintering temperature -, or rather that we make these observations after interrupted sintering tests. In that case, one must pay attention that these interruptions do not bring additional interference to the observations (cooling rate high enough to efficiently stop quickly all the mechanisms related to the diffusion of species, but low enough to avoid any cracking). The most pertinent parameter to follow through these interrupted tests is the surface fraction of porosity, which equals the volume fraction of porosity, provided that the material is stationary in a statistical sense. Therefore, we will associate the speed of deformation, hence the densification rate, with the evolution of the porosity versus time drawn from interrupted tests (Costa et al, 2009; Costa, 2009). 2D porosity information can easily be evaluated by SEM observations of polished surface after appropriate segmentation and binarization; better, 3D information can directly be obtained by microtomography (Costa et al, 2009). Experimental preparation of the samples for the analysis of interrupted tests is quite straightforward when exploring the end of

the sintering, but is quite delicate at the onset of the consolidation, *i.e.* just after the plateaus for the calcination of the binders. If non-consolidated samples are embedded in resin prior to observation (Fig. 10), one must pay a careful attention on the choice of the polymer that must not retract significantly, otherwise the surface (or volume) fraction of pores will be highly underestimated.

Observation of the microstructure after interrupted tests has allowed us to detect an unexpected second order deformation mechanism, that acts also in single layers (in that case, no differential shrinkage kinetic between different materials can possibly be invoked): this mechanism originates from a shrinkage kinetic difference within the anode itself associated with a porosity gradient (from the top to the bottom of the sample) that is caused by the sedimentation of the larger BCY10 grains from the moment the tape is cast until it is totally dried (Fig. 11). The effectiveness of the slurry stability is essentially a function of the grains surface since electrostatic forces intensity derived from the adsorbed species. Large grains present an unfavourable surface/volume ratio in that respect, and then are more sensitive to gravity. This effect is effective when the grains size distribution is not narrow enough, and it aggravates the differential shrinkage kinetics when multilayers are concerned.

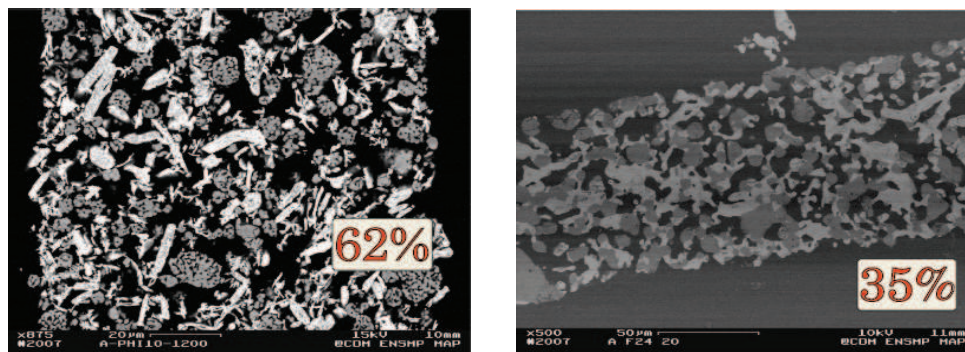
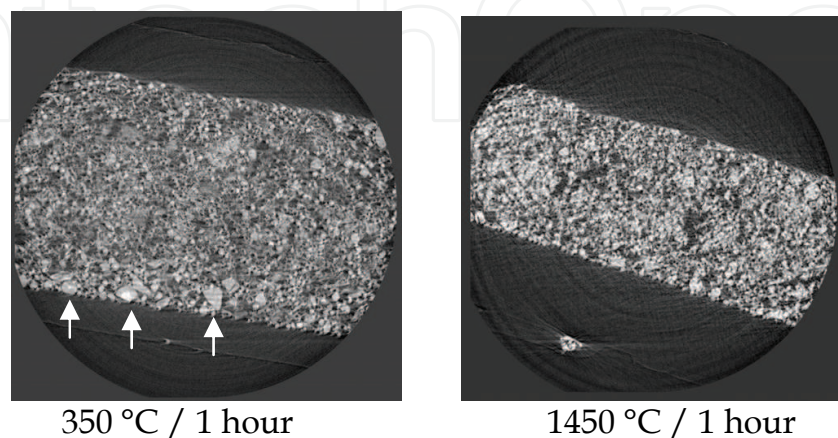


Fig. 10. SEM observation of the polished surface of a PCFC anode (50 vol.% BCY10 = white phase + 50 vol.% NiO = grey phase; dark areas are porosity) taken from the same dried green tape about 100 μm thick; left: test was interrupted at 1000 $^{\circ}\text{C}$ during heating (surface fraction or pores = 62%); right: test was interrupted after 10 hours at 1450 $^{\circ}\text{C}$ (surface fraction of pores = 35%); scales are on the micrographs; note the large shrinkage of the thickness (Costa et al, 2009; Costa, 2009)



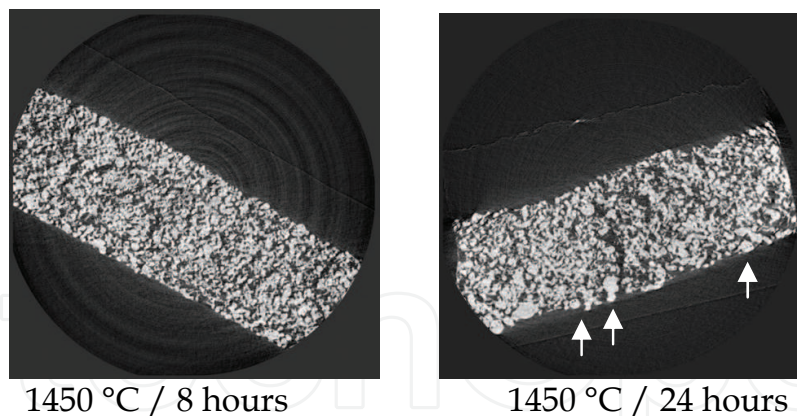


Fig. 11. Morphology of a PCFC anode (50 vol.% BCY10 + 50 vol.% NiO = white phase; dark areas are porosity); 2D surfaces taken from 3D microtomography (ESRF, Grenoble, France) corresponding to interrupted sintering tests; initial anode thickness = 250 μm , upper surface during test is up on the micrographs; sedimentation of large BCY10 grains is easily detected at the bottom of the anode, especially on the top left and bottom right images; note the high level of shrinkage of the thickness (Costa et al, 2009; Costa, 2009)

Owing to the transport of matter during sintering (diffusion, visco-plastic flow, densification...), one may assume that the multilayer is free of stresses at the end of the sintering plateau. When the flatness of the multilayer is maintained by a weight, thermo-elastic stresses due to thermal expansion mismatch and different elastic constants will develop upon cooling, which will cause either remnant deformation or cracking when removing the weight. When the flatness is maintained by counterbalancing the deformation (in multilayers with an odd number of components) during all the length of the plateau, residual deformation will also develop. In either cases this residual deformation can be eliminated to a certain extent by playing again on the layers thickness if possible, and/or on the apparent Young's modulus, *i.e.* by the addition of more pore formers (Grosjean, 2004).

3. Experimental examples

3.1. Aqueous tape-casting of SOFCs

We have used standard commercial powders for this study [6] as described below:

- Electrolyte: YSZ (TZ8-Y, Tosoh),
- Anode: porous Ni-YSZ cermet (Ni precursor = NiO, Novamet A Type),
- Cathode: composite YSZ-La_{0.80}Sr_{0.20}MnO_{3- δ} (LSM, Rhodia).

Following what has been extensively discussed above, the slurry composition for each layer was formulated to obtain the same final shrinkage for the three components of the cell; the thickness of the cast tape was adjusted so that the thermoelastic mechanical stresses were minimized during the cooling following Timoshenko's bilayer model (Timoshenko and Gere, 1991). The slurries composition was based on the following chemicals:

- Water (solvent)/sodium alginate (binder) in the ratio (100:1),
- Dispersant: Dolapix ET85 (droplets),
- Macro pore-former when needed: acrylic polymer.

Slurries for the electrodes and for the electrolyte were cast separately, with appropriate thickness, on a glass support. Green tapes were then obtained by the chemical gelation of the sodium

alginate through the complexation of Ca^{2+} ions in the presence of a CaCl_2 solution. The three different green tapes were then cut and stacked to obtain a full green single cell. The three-layer stacks obtained in this way were then dried between two hydrophilic honeycomb supports at 70°C so that the water could be desorbed symmetrically from the two surfaces to avoid any warping of the stack. After the drying was completed, the stacks were placed between two Mullite alveolar supports, whose weight was appropriate to maintain the flatness of the cell without interfering with the planar shrinkage. Two-inch flat SOFC single cells with high quality interfaces between electrolyte and electrodes were routinely obtained after sintering at 1350°C for 8 hours (Fig. 12 and Fig. 13).

Nevertheless, co-sintering the whole cell at 1350°C led to poor electrochemical properties owing to reactivity between YSZ and LSM [6,18]. In that specific case, we have developed a sequential organic tape-casting approach to cast the cathode layer on top of an already sintered Anode/Electrolyte half-cell prepared by the water based process described above. It is to be noted here that, owing to surface tension considerations, water-based tape-casting does not lend itself to the successful deposit of a layer on top of an already sintered material. With this method the cathode could be heat-treated at a lower temperature (1200°C for 1 hour), conditions where reactivity with YSZ does not appear significant.

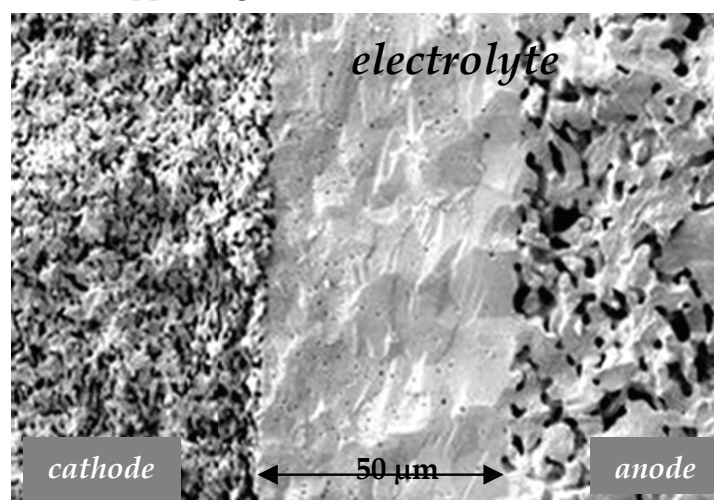


Fig. 12. SEM observation of a cross section of a SOFC (YSZ + LSM/YSZ/YSZ + NiO) obtained by tape-casting (from Grosjean, 2004)

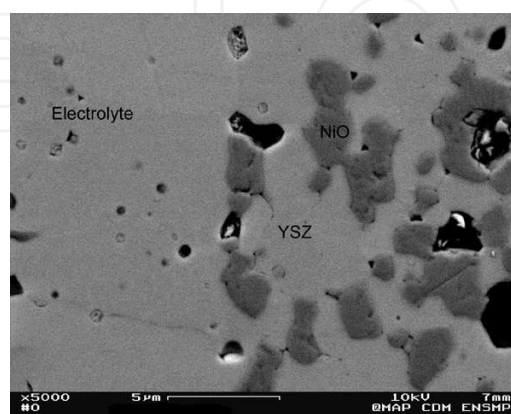


Fig. 13. SEM observation of a polished cross section of the interface between the anode and the electrolyte in a SOFC (YSZ + LSM/YSZ/YSZ + NiO) obtained by tape-casting (from Grosjean, 2004)

3.2. Organic tape-casting of PCFC

In this study only the fabrication of bi-layers or symmetrical cells Anode/Electrolyte/Anode was attempted since no cathode material for PCFC was available at this time (Costa et al, 2009; Costa, 2009). The following materials were either home made or commercially supplied:

- Electrolyte: BCY10 was produced via a chemical route based on oxalate co-precipitation following exactly the procedure described by Almeida de Olivera et al (Almeida de Oliveira et al, 2007),
- Anode: porous Ni-BCY10 cermet (Ni precursor = NiO, Novamet A Type) in the volume ratio 1:1 (corresponding weight ratio = 1:1.08).

Water-based tape-casting was not applicable for BCY10 shaping because BCY10 exhibits a strong basic behaviour; since water is an amphoteric electrolyte, the pH of such a suspension is quite high and hydrolysis of the material occurs rapidly. Therefore, tape-casting of PCFC based on BCY powder must be carried out with an organic solvent totally deprived of water. Among all of the organic solvent/binder possible couples, we have chosen the couple Ethanol/PVB: it limits the toxicity of the slurries and makes BCY10 suspensions stable rather easily. The following products were used:

- Absolute Ethanol (Fisher Scientific),
- Poly(Vinyl Butyral) (PVB) (Acros Organics) as the binder (and as a pore former for the anode),
- PolyEthylene Glycol-400 grade (PEG) (Fisher Scientific) as the plasticizer.

Table 1 below gives the quantity of products for the electrolyte and anode slurries for a typical tape-casting experiment; the compositions are optimized for the anode and electrolyte in respect with the desired final microstructures (dense BYC10, porous anode with interconnected Ni particles, BCY10 and network of pores). Slurries were ball-milled for 4 hours prior to casting in order to obtain homogeneous suspensions.

Slurries were cast on a glass support coated with glycerol to prevent the adhesion of the green tapes. First a 500 μm thick anode layer was cast, and left twenty minutes at room temperature for the drying process to start taking place. Then a 150 μm thick electrolyte layer was cast on top of the anode tape. For the fabrication of symmetric half-cells, a second 500 μm thick anode layer was cast on top of the electrolyte layer, again twenty minutes later. The stack of green tapes was then dried at room temperature for two hours before being cut into discs. Since BaCeO_3 based perovskite reacts at high temperature ($> 1200^\circ\text{C}$) with most of the materials used as sintering supports (Al_2O_3 , ZrO_2), the sintering of BCY10 was made on a BCY10 powder layer. After a plateau of 1 hour at 350°C for burning the organic products, the sintering was carried out at 1450°C for 24 hours for a full densification of the electrolyte (Fig. 14 and Fig. 15).

Chemicals	Anode / g	Electrolyte / g
BCY10	2.5	6.0
NiO	2.7	-
Ethanol	4.5	4.8
PVB	2.0	0.60
PEG	0.70	0.30
Glycerol	0.45	-

Table 1. Composition (in g) of optimized slurries in regards to the final microstructure

Flat symmetrical half-cells 20 mm in diameter were routinely obtained via this procedure. Bi-layers anode/electrolyte could not be obtained without a very strong warping for the reasons discussed in section 2.3. Solutions range from narrowing the BCY10 grain size distribution, adding an effective dispersant to the slurry, or compensating the deformation by that of the cathode when such material is available.

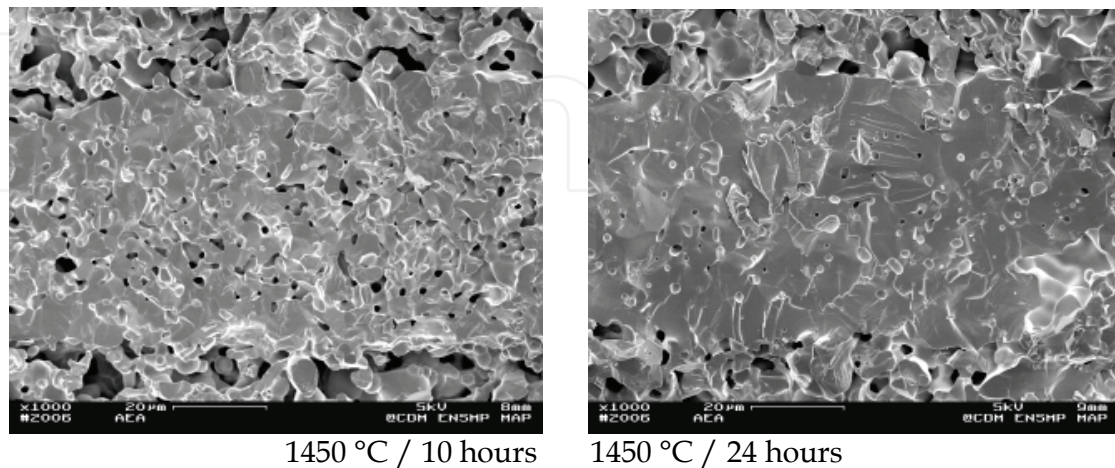


Fig. 14. SEM observation of a cross section of a PCFC half-cell anode/electrolyte/anode sintered at 1450 °C for different durations (from Costa et al, 2009; Costa, 2009)

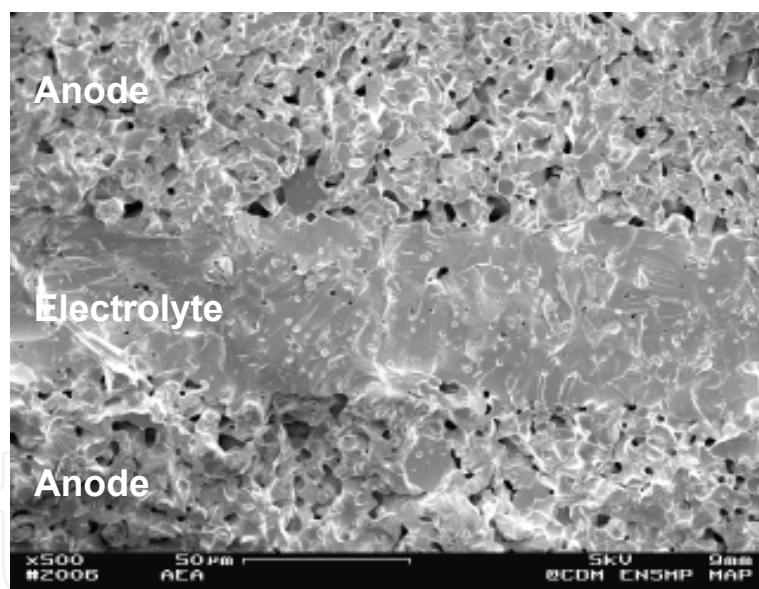


Fig. 15. SEM observation of a cross section of a PCFC half-cell Anode/Electrolyte/Anode sintered at 1450 °C (from Costa et al, 2009; Costa, 2009)

3.3. First realizations of IDEAL-Cell

This new innovative concept is described here, and its characteristics, specificities and advantages compared to SOFCs and PCFCs are given. This concept has just reached the Proof of Concept step at the end of the year 2009, in the frame of a 4-years FP7 European project. The major difference of this concept compared to the others is that it is based on a central porous membrane that displays a mixed conduction (proton and oxygen). This section will show how tape casting is applied to shape the different elements of this new cell.

The basic ideas behind the IDEAL-Cell concept consists in isolating the hydrogen and oxygen compartments from the exhaust water to avoid the main problems associated with the presence of water at electrodes in SOFC (Fig. 1) and in PCFC (Fig. 2). In the IDEAL-Cell design each compartment has a single role to play, for which it can be fully optimized. Such a three independent compartments system is being developed by an European consortium (ARMINES, France; Université de Bourgogne, France, CNR, Italy; DLR, Germany; IEES, Bulgaria; AGH, Poland; Marion Technologies, France; Naxagoras, France; Visimbel, Germany) by joining the cathode part of a SOFC to the anode part of a PCFC, rejecting thus the production of water toward a common central compartment (Fig. 3). The protons created at the anode side and the oxygen ions produced at the cathode side diffuse through the corresponding electrolytes toward the central membrane, where they combine. The electrons that are torn off atomic hydrogen at the anode will go to the external circuit and feed atomic oxygen to create oxygen ions at the cathode side. The central membrane is a mixed proton and oxygen composite conductor with highly porous microstructure to allow the evacuation of water.

Unlike in SOFCs and PCFCs, this design will avoid gas dilution, condensation of water on the catalytic sites, inhibition of mass transfer, corrosion by oxygenized water at high temperature. In addition, it allows for an easy and independent application of gas pressure on both electrodes to enhance the overall efficiency. The concept, patented by ARMINES/Mines-ParisTech, has been proved in 2009 via four criteria: i/ a stable OCV, ii/ a stable polarization curve, iii/ complex impedance fingerprint typical of water formation, iv/ measurement of water formation as a function of the current across the cell. Up to now, as first attempts to prove the concept, different processes have been implemented (SPS, HP, tape casting) (Thorel et al, 2009a; Thorel et al, 2009b, Presto et al, 2009); the shaping technique developed at ARMINES/Mines-ParisTech (Abreu, 2011) is based on the cold-pressed and sintered BCY electrolyte support, on which all additional layers are deposited by tape-casting (Fig. 16). The cell is not yet at all optimized and is still very thick for experimental purposes (about 2 mm), but already shows highly attracting performances (5 mW/cm^2). Extrapolation towards typical cell thickness indicates that the level of performances attained by IDEAL-Cell after 2 years of operation of the project is even better than that of PCFCs. In addition, modelling shows that the concept exhibits very little electrodes overpotentials and extremely high potentialities for improvements.

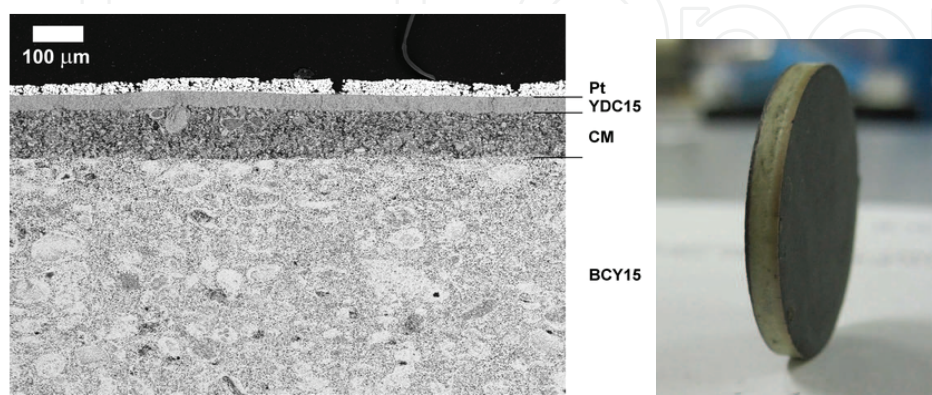


Fig. 16. Left: SEM observation of a cross section of the IDEAL-Cell Proof of Concept sample with Pt electrodes; right: full BCY supported IDEAL-Cell with : cathode = LSCF; oxygen

electrolyte = YDC15; central membrane = YDC15 + BCY15; proton electrolyte = BCY15; anode = BCY15 + Ni (Abreu, 2011)

4. Conclusion

High temperature fuel cells are very sophisticated objects, and as such are very complicated to shape. The fabrication costs constitute the major brake to their development in a highly competitive segment where competitor alternative power sources progress at a high rate. Decades of efforts and accumulated knowledge on one of the most known ceramic (Zirconia) did not allow putting yet a low cost operating SOFC on the market.

Taking into account the numerous parameters that define the operability of a process such as tape-casting for shaping ceramic fuel cells becomes very difficult. Empiricism should be backed by modelling and computer simulation, which is far from being routinely available for processes in general, and tape-casting in particular.

One must also pay attention to the fact that cutting the fabrication costs at any prices is not necessarily a good option since it may raise unexpected issues (*i.e.* co-sintering); rather, a sequence of compatible processes can be an efficient solution (*i.e.* coupling tape-casting with screen-printing and/or plasma spraying...). The community should also be imaginative and open to innovative solutions that may be less energy efficient but infinitely simpler (monochamber concept), or a bit more complicated to fabricate but having enormous advantages (IDEAL-Cell).

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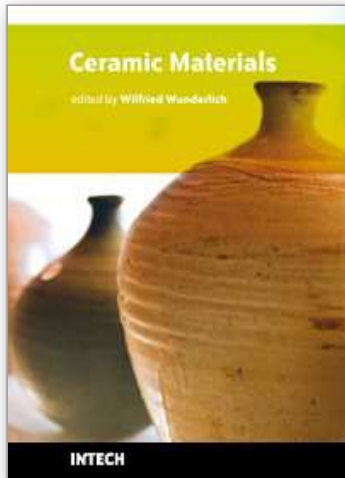
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