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Influence of pore formers on slurry composition and microstructure of tape cast supporting anodes for SOFCs

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Abstract

Nickel–yttria stabilized zirconia cermet (Ni/YSZ) is the most common material for supporting anodes in fuel cells applications. The microstructure of this element is crucial for the performances of the entire fuel cell. For this reason, four different pore formers (graphite, carbon black, rice starch, potato starch) and a surplus of organic binder were considered for its optimization. Their influence on the amount of porosity and on the pore dimensions and shape as well as the effect on the composition of the tape casting slurry was analysed. The study allowed identifying rice starch and carbon black as the most promising pore formers for the production of large area (10 cm × 10 cm) supporting anodes for SOFC application.

Keywords: SOFC; Supporting anode; Tape casting; Pore formers; NiO/YSZ

1. Introduction

Solid oxide fuel cells (SOFCs) have recently attracted great attention for their ability to convert the chemical energy of a fuel (hydrogen, natural gas, etc.) directly into electrical energy. This conversion is characterized by high efficiency and low greenhouse gas emissions. Like batteries, fuel cells consist of an electrolyte sandwiched between an anode and a cathode, but unlike them they operate as long as the fuel is supplied.[1] Among the all possible SOFC designs, the anode-supported flat one is perhaps the most promising. In this design a very thin (~15 μm) electrolyte film is deposited on a supporting anode of 800–1500 μm made by tape casting or die-pressing.[2]

Porous nickel–yttria stabilized zirconia (Ni/YSZ) cermet is currently the most common anode material for SOFCs applications.[3] In this cermet, Ni acts as a catalyst for the oxidation of H_2, whereas YSZ forms the porous ceramic network required to create an extended reaction zone and to adapt the thermo-mechanical properties of the anode to the ones of the other cell components. The microstructure of the supporting anodes is crucial for the performances of the entire cell. The porous ceramic network has to provide the mechanical strength to the fuel cell and to allow an easy flow of the gases to and from the electrolytic membrane, whereas the nickel particles should be homogeneously distributed to form a well-extended matrix to enhance the catalytic activity of the anode.

It is well known that either gas permeability and electrical conductivity of SOFC anodes are strongly dependent on microstructural parameters such as porosity, phase distribution and particle size.[4–6] For this reason a careful control of the microstructure is crucial for the optimization of the electrochemical performance of the anode.

The starting powder for Ni-based components generally consist of a mixture of NiO and YSZ. The former is then reduced to metallic nickel *in situ* when the anode is exposed to the fuel during cell operation.[7] Although this reduction increases the total amount of porosity,[8] the final value is not generally high enough to fulfil the anode requirements. For this reason it is common practice to introduce a pore former which improves access to the active three-phase boundary region of the anode.[8–10]

Tape casting represents a well-established technique to obtain large ceramic sheets with good surface finish and thickness in the range 0.1–1.5 mm.

Although several studies exist on the effect of the amount of pore formers on the properties of the anodes little has been reported on the influence of their nature on the tape casting slurry and on their final porosity.

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Aim of this work was to study the influence of the morphology of four different pore formers on the tape casting formulation and on the amount and shape of porosity of the fired body in order to obtain a microstructure suitable for SOFC applications.

2. Experimental

Commercial NiO (JT Baker, USA, mean particle size of 1.0 μm and specific surface area (SSA) = 4.0 m^2/g) and 8 mol% yttria-stabilized zirconia (YSZ) (TZ8Y, Tosoh Co, Tokyo, Japan, mean particle size of 0.3 μm and SSA = 20.0 m^2/g) were used as starting materials.

The pore formers were selected taking in consideration the particle shape and size, the decomposition with minimal residue at reasonably low temperatures, and the compatibility with the other materials in the anode. Four compounds were selected: (i) potato starch (PS, Sigma–Aldrich), (ii) rice starch (RS, Sigma–Aldrich), (iii) carbon black (CB, Thermax), (iv) graphite (GR, Sigma–Aldrich). In addition, the influence of an additional amount of organic binder was evaluated.

All the formulations were prepared by mixing the desired amounts of nickel oxide, YSZ and pore former with the azeotropic mixture of methyl ethyl ketone (MEK, Sigma–Aldrich) and ethanol (EtOH, Sigma–Aldrich) as solvent and glycerine trioleate (GTO Fluka) as dispersant. The ratio of NiO/YSZ was kept at 70/30 vol%. Poly-vinyl-butyral (PVB) (Butvar B98, Monsanto Co. St. Louis, MO, USA) was selected as binder and polyethylene glycol (PEG-400, Fluka) and benzyl butyl phthalate (BBP) (S160, Monsanto Co., St. Louis, MO, USA) were used as plasticizer in 1:1 weight ratio.

Standard colloidal processing technique was used for the preparation of the tape casting slurry. In the first stage solvent and dispersant were mixed with NiO powder by ball milling in polyethylene jar for 24 h to ensure good dispersion. The binder and the ZrO_2 powder were added in a second stage to allow a better homogenisation with NiO. Additional 24 h of ball milling were necessary when additional binder was used. In the third step the plasticizers were added together with the pore former and milled for 24 h. The mixed suspension was deaired under vacuum and casted on a Mylar carrier to obtain green tapes of dry thickness of about 700 μm.

The green tapes were cut and subsequently sintered in air at 1200 °C for 2 h. Dimension and weight of the green and sintered tapes were measured to determine their density and degree of sintering. All the sintered samples were analysed by SEM (Stereoscan 360, Cambridge Instruments, UK) and by mercury porosimetry. For this latter analysis a low-pressure porosimeter was used in combination with a high-pressure one (Pascal 140 and 240 series respectively, Thermo Finnigan, Waltham, MA, USA) to allow accurate measurements of pore size ranging from macropores (hundreds of microns) down to mesopores (lower limit: 4 nm).

3. Results and discussion

3.1. Slurry formulations

Fig. 1 shows the morphology of the different pore formers considered in this study. They differ from each other mainly with respect to: (i) origin (organic or inorganic); (ii) particle shape; (iii) particle size distribution.

Organic pore formers such as potato and rice starch differ with respect to shape and dimension and are characterized by dense particles of well-defined shape (Fig. 1a and b). On the other hand inorganic additives are formed by aggregates of nanometric particles or sub-micronic dense lamellae as shown in Fig. 1c and d for carbon black and graphite, respectively. These aggregates can be easily broken down during the ball milling process leading to powders with a broad particle size distribution.

The porosity induced by an additional amount of binder is not influenced by the binder morphology as it is dissolved by the solvent. Therefore, the increased volume of the binder results in a uniform microporosity as a consequence of its homogeneous distribution in the liquid phase.

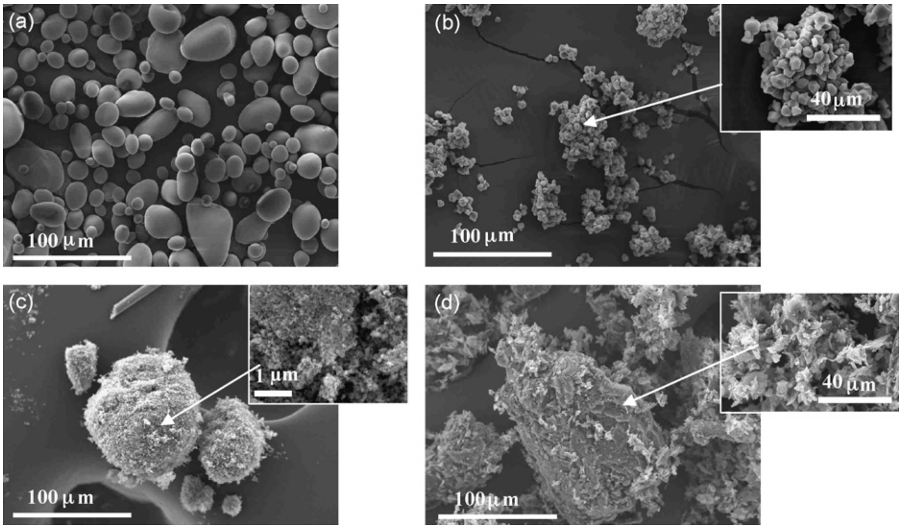

Fig. 1. SEM micrographs of the different pore formers used: (a) potato starch, (b) rice starch; (c) carbon black and (d) graphite. The insets are high magnification micrograph to show the different morphology of the pore formers.

Table 1
Volume composition of the slurries (vol%) and the green tapes (vol$_g$%)

Tape	Powder		Dispersant		Binder		Plasticizer		Solv.	Pore former	
	vol%	vol$_g$%	vol%	vol$_g$%	vol%	vol$_g$%	vol%	vol$_g$%	vol%	vol%	vol$_g$%
T	20.7	51.6	1.4	3.6	9.1	22.6	8.9	22.2	59.9	0	0
B	16.1	46.5	1.1	3.3	6.6	11.0	7.4	21.2	65.3	3.5	10.0
PS	18.7	45.2	1.5	3.5	8.6	20.8	8.4	20.4	58.6	4.2	10.1
RS	18.7	45.2	1.5	3.5	8.6	20.8	8.4	20.4	58.6	4.2	10.1
GP	17.4	43.6	1.3	3.4	8.6	21.7	8.6	21.2	60.1	4.0	10.1
CB	15.9	40.8	1.1	2.9	9.1	23.4	8.9	22.8	61.1	3.9	10.1

T: tape without pore former; B: additional binder as pore former; PS: potato starch; RS: rice starch; GP: graphite; CB: carbon black; Solv.: solvent (MEK + EtOH).

All the pore formers were added in 10 vol% on dry green tape basis to study the influence of the morphology and nature of the pore former on the amount and shape of final porosity.

The dispersion characteristics of the pore formers greatly influence the viscosity of the slurry and the final properties of the green tape. The NiO–YSZ slurry formulation was then adjusted in order to obtain: (i) a slurry with suitable viscosity for the casting process and (ii) a flexible and crack-free green tape.

The method suggested by Corbin and Apté[11] was chosen as a starting point for the optimization of the slurries. In this method the pore formers are considered as additional ceramic powder and the formulation without pore formers is adjusted keeping the weight ratio (total amount of organics in the green tape):(ceramic powder + pore formers) constant. This approach was not able to satisfy the two constraints presented above and stressed the influence of the pore formers nature on the tape casting slurry. The starches induced a huge increase of the viscosity hindering the subsequent casting process. On the other hand, the same approach applied to slurries with graphite or carbon black produced green tapes brittle and with lots of cracks. A peculiar behaviour was observed for the slurries using carbon black. This pore former caused a sudden increase in slurry viscosity just after its addition; the viscosity then decreased during the ball milling process reaching acceptable values just prior casting.

Two different properties of the pore formers are thought to influence the tape casting slurry: the particles dimensions and the nature of the aggregates. The amount of solvent and organics needed for a tape casting slurry strongly depends on the nature and dimensions of the particles to disperse.[12] Meier et al.[13] showed that nanometric particles need much more organics than the micrometric ones due to the adhering layer of organics on their surface (responsible for their dispersion) that becomes more important as the dimension of the particles decreases.

In the case of starches, the primary particles are bigger than the ones of the powders and having less surface area they require less amount of organics to be dispersed and to form a proper organic network. On the other hand, graphite and carbon black have a very fine fraction that requires a higher amount of organics than the NiO/YSZ powder.

The morphology of the carbon black aggregates is thought to be responsible for the change in viscosity observed during the preparation of the slurry. Their sponge-like structure "traps" the solvent as soon as the pore former is added to the slurry, increasing in this way its viscosity. The solvent is then slowly "released" as the aggregates are broken down during the ball milling process. This effect is confirmed also by the SEM picture of the sintered body (Fig. 4d) that shows pores with dimensions more similar to the one of the primary particles than that of the aggregates. When an additional amount of binder is used to increase the porosity (tape B) more solvent is obviously needed to promote its dissolution.

From these considerations, the initial slurries were modified adjusting the amount of solvent and organics taking into account the morphology of the aggregates, the primary particles dimensions and the pore former nature. The results of this optimization process are presented in Table 1.

To better discuss the data, the two most important parameters considered in the optimization of the tape casting slurry are

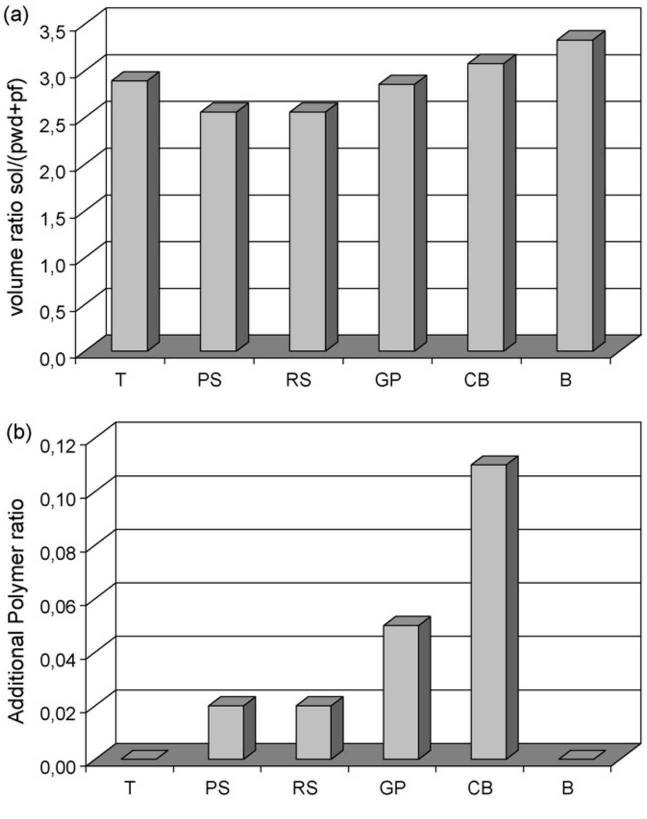

Fig. 2. (a) Solvent to (powder + pore former) volume ratio for each system analysed. (b) Additional polymer ratio (AP) needed.

Table 2
Main characteristics of the green and sintered tapes

Tape	ρ_{green} (g/cm^3)	ρ_{green} (th) (g/cm^3)	Shrinkage (%)	ρ_{sint} (%)	Porosity (%)	d_{50} (μm)
T	3.67	3.85	10.4	66	37.8	0.35
B	3.43	3.57	14.5	68	26.8	0.45
PS	3.35	3.54	10.1	58	42.3	0.44
RS	3.35	3.54	10.2	58	40.0	0.27
GP	3.38	3.54	8.2	54	46.0	0.29
CB	2.98	3.43	11.3	49	48.3	0.29

ρ_{green} (th): theoretical green density.

presented in Fig. 2: (a) the solvent to (powder + pore formers) volume ratio and (b) the so-called additional polymer.

The first parameter is linked to the amount of solvent needed to obtain slurry of suitable viscosity for casting. Fig. 2a shows that the amount of solvent is not only function of the dimension of the pore former particles but also of its nature. As expected, the large starch particles need less amount of solvent than the ceramic powder whereas the fine particles of carbon black requires a large amount of solvent to be dispersed. Graphite is composed by either large and small platelets and its behaviour is somewhere between the previous two. As already mentioned, a higher amount of solvent is also needed to dissolve the additional binder used in B.

The graph of Fig. 2a stresses also the different behaviour of inorganic and organic pore formers.

While graphite and carbon black need different amount of solvent as a consequence of their different particle size, the solvent required by the two starches seems not to be influenced by the particle dimensions. The same situation is reflected in Fig. 2b.

The introduction of a pore former requires an additional amount of organics to disperse it. This quantity is indicated by Corbin et al.[14] as additional polymer ratio (AP) and it is calculated through the equation:

$$\text{AP} = \frac{[V_{\text{P}} - V_{\text{C}}(48.36/51.64)]}{V_{\text{T}}}$$

where V_{P} is the volume of polymer (deflocculant + binder + plasticizers) in the pore former/NiO–YSZ composite, V_{C} is the volume of ceramic powder in the composite, V_{T} is the total green volume and 48.36/51.64 is the volume ratio of polymer to NiO–YSZ in the tape without pore former. AP gives an indication on how much the pore former influences the organics content (binder, dispersant and plasticizers) of the tape casting slurry.

Fig. 2b clearly shows that the introduction of carbon black or graphite in the slurry must be counterbalanced by an increase in the organic content in order to obtain a crack-free green tape. The level of this increase is linked to the size of the pore former particles: smaller the particles higher the amount of organics needed. On the contrary, the addition of starches induces a small variation in the slurry and this variation is independent on the particle size of the pore former.

From these data it can be concluded that beside the size, also the nature of the pore former plays an important role on the tape casting slurry.

Inorganic pore formers (like graphite and carbon black) seem to behave like ceramic powders: the composition of the pure ceramic slurry has to be modified to allow their dispersion and the formation of a stable network with the organics.

The starches on the contrary, do not interact very strongly with the other components of the suspension showing behaviour more similar to an organic additive than to that of a ceramic powder. In this respect, they need much less solvent to be dispersed (also in account of their bigger dimensions) and a little amount of organics to be integrated in the green tape matrix.

3.2. Green and sintered tapes

The different interaction of the pore formers with the organics is reflected also on the values of green density and porosity of the tapes obtained.

In Table 2 the values of density (of the green and sintered bodies), shrinkage, porosity and mean pore diameter (d_{50}) for all the systems are reported. The values are the mean of 10 different samples and are affected by errors of 2%. The mean pore diameters have been measured by mercury porosimetry and represent equivalent pore size based on cylindrical tube model generally considered for evaluation.

The theoretical value of density of the cermet (6.42 g/cm^3) is calculated as weighted average of the densities of NiO and YSZ, whereas the theoretical green density is based on the dry components of the green tape assuming there is no void space in it and that the evaporation of the organic solvent in the suspension is complete.

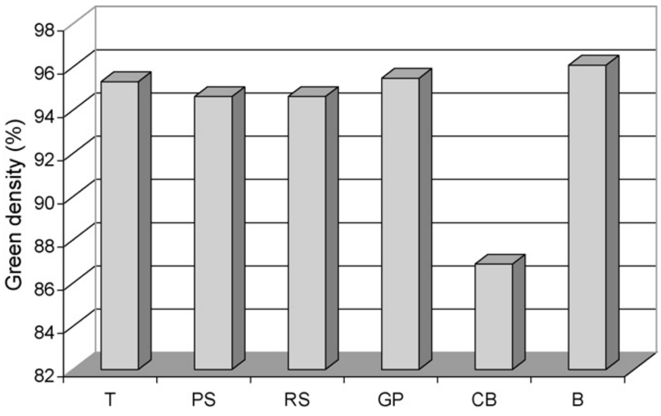

Fig. 3. Percentage of green density of the tapes.

The effect of the pore formers on the green density of the tape is presented in Fig. 3. All the tapes have green density around 95%, in agreement of what already noticed by Corbin and Apté. The system with carbon black, however, presents an unusual low density. This can be due to the influence of the pore former on the packing density of the NiO–YSZ powders or to an incomplete evaporation of the solvent from the tape. This last effect could be linked to the "sponge effect" introduced previously and it was confirmed by a pungent smell of solvent coming from the surface of the green tape.

Corbin and Apté suggested that the values of shrinkage and porosity after sintering, could give an indication on the microstructure of the green tape with a pore former. They assumed that the pore former and the ceramic powder develop a well-defined packing density and distribution into the polymer matrix of the green tape formed by binder, dispersant and plasticizers.

They identify three different situations:

(a) the pore former is introduced in the ceramic slurry without organic compensation: in this case there is no alteration of the ceramic particles packing and the volume fraction of the final porosity will be equivalent to the volume fraction of the pore former introduced;

(b) an extra organic (AP) is introduced to disperse the pore formers and it distributes itself on the surface of the pore former: in this case there is an increase of the ceramic powder packing density that causes a reduction in sintering shrinkage whereas the final porosity is due to the sum of the volume of pore former *plus* the volume of AP;

(c) an extra organic (AP) is introduced to disperse the pore formers but only a part of it is used for this purpose; the remainder distributes itself throughout the rest of the green tape: in this case there is an increased shrinkage percentage and a value of final porosity sum of the volume of the pore former and organics introduced.

In the case of potato and rice starch the shrinkage is consistent with the one of the NiO–YSZ tape whereas the values of porosity correspond to the volume of pore former added (≈10%). For these pore formers then, the AP does not induce any additional porosity probably because its amount is so low to be included in the experimental errors. The microstructure of these tapes is presented in Fig. 4b and c: both the micrographs

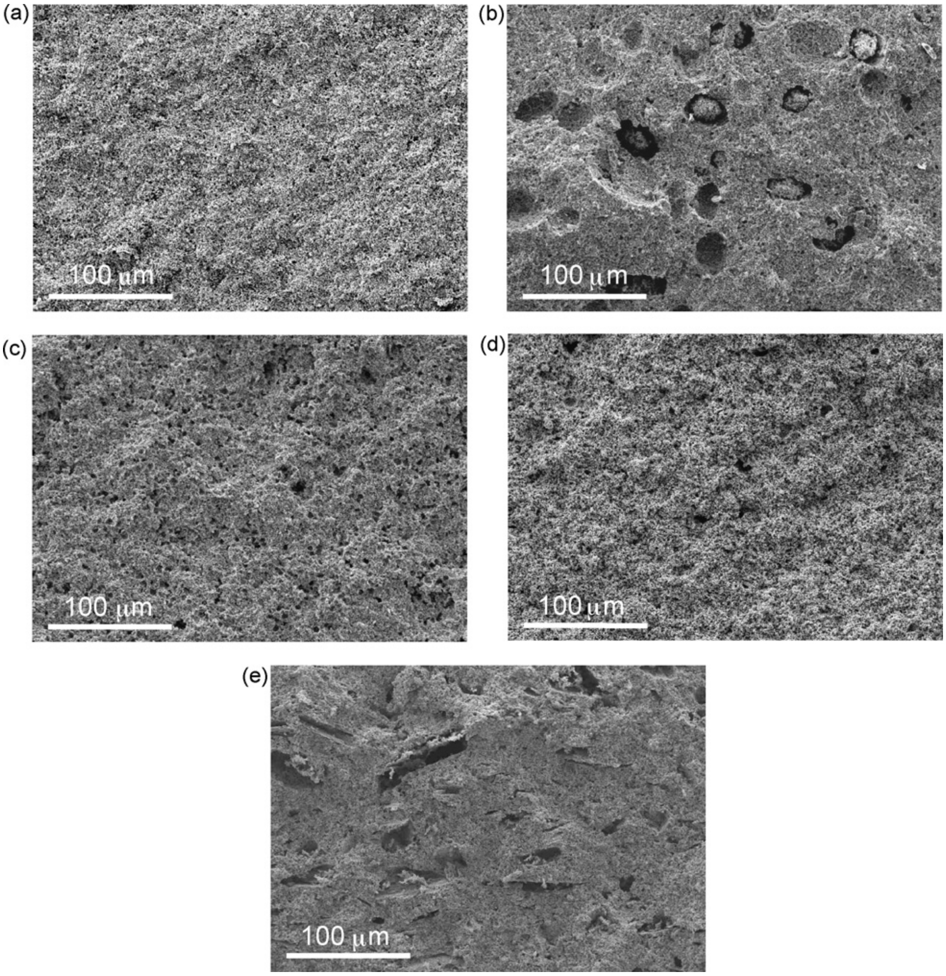

Fig. 4. SEM micrographs of the sintered tapes: (a) without pore former; (b) with potato starch; (c) with rice starch; (d) with carbon black and (e) with graphite.

shows pores resembling the shape and dimension of the pore former introduced confirming the assumption previously made.

The tape with graphite presented a lower shrinkage compared to the one of NiO–YSZ and a slightly higher porosity compared to the one of the tapes with starch. This behaviour suggested that the organics distribute on the surface of the graphite. The value of porosity can be justified examining the SEM micrograph of the sintered tape (Fig. 4e). The ball milling process has little effect on the graphite particles. The big platelets are still present at the end of the process and therefore could lower the packing efficiency of the NiO–YSZ powders leading to higher values of porosity than expected as already noticed by Messing and Onoda.[15]

For carbon black, the high value of shrinkage clearly indicates a decreasing of the ceramic packing density (case c). The SEM micrograph of the sintered tape (Fig. 4d) suggested a possible explanation for the high value of porosity. As previously introduced, the aggregates of this pore former are broken down during the slurry preparation, leaving very fine primary particles. In this situation, it is not possible to adopt the model of Corbin and Apté because they assume pore formers of much higher dimension than that of the ceramic powder. It is however plausible to assume that the sub-micronic carbon particles distributes themselves on the surface of the bigger ceramic powder hindering in this way their sintering process and increasing the final value of porosity of the sintered tape. The use of an additional amount of binder increases the shrinkage and decreases the final porosity. This is thought to be due to an increased level of freedom of the particles in the organic matrix that lead to an higher packing density and, as a consequence, a lower value of final porosity. This effect can be exploited in the co-firing process of anode and electrolyte to improve the sinterability of the electrolyte.

It is worth noticing that the values of porosity geometrically calculated are consistent with the ones coming from the porosimetry. This is a clear indication that the porosity of the sample is all opened. This is particularly important for SOFC applications where the reactants and products need to flow to and from the electrolyte. In this respect the shape of the porosity is almost as important as its total volume.[7,16–18] The micrographs of Fig. 4 shows that the porosity produced by graphite and potato starch is not suitable for SOFC application: the first is perpendicular to the direction of gas flow, whereas the second is mainly due to ink bottles. The latter is less efficient for the flowing process because only a small part of it can be actually used by the gas for the permeation process as already noticed by Simwonis et al.[19] On the other hand, the use of rice starch or carbon black leads to channel porosity particularly useful for this kind of application. Samples of NiO–YSZ tapes and tapes obtained with rice starch and carbon black have been reduced and mechanical strength and permeability measurements are in due course.

4. Conclusions

Different pore formers were chosen in order to study their influence on the tape casting slurry formulation and on the final porosity of the tape. The choice was done on the basis of their nature (organic or inorganic) and morphology (particle size, shape and structure of the aggregates).

The study allowed to identify the right way to modify a tape casting slurry taking in account for the nature and dimension of the pore former. Rice starch and carbon black were identified as the most suitable pore formers for the production of anodes for SOFCs by tape casting whereas an excess of binder can be used to promote their shrinkage.

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