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Fuel Cell: A Review and a New Approach About YSZ Solid Oxide Electrolyte Deposition Direct on LSM Porous Substrate by Spray Pyrolysis

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1. Introduction

Environmental concerns related to energy, already widely held today, will substantially increase in coming years. The energy is one of the main factors to consider in environmentalists discussions, since there is an intimate connection between energy, environment and sustainable development (Stambouli & Traversa, 2002a). In response to a critical need for cleaner energy technology, the solutions have evolved, including energy conservation by improving the efficiency of global energy, a reduction in the use of fossil fuels and an increase in the supply of renewable energies (hydro (Mendez et al., 2006), solar (Akorede et al., 2010), wind (Mendez et al., 2006), biomass (Kirubakaran et al., 2009), geothermal (Fridleifsson, 2001), hydrogen (Louie & Strunz, 2007), etc…). In the context of renewable energy, a good alternative can be found in the development and popularization of fuel cells (Akorede et al., 2010).

A fuel cell is an energy conversion device that generates electricity and heat by combining, electrochemically, fuel gas (hydrogen, for example) and an oxidant gas (oxygen in air). During this process, water is obtained as a reaction product. The fuel cell does not work with charging system such as a battery, it only produces power while the fuel is supplied. The main characteristic of a fuel cell is its ability to convert chemicals directly into electrical energy, with a conversion efficiency much higher than any conventional thermo-mechanical system, thus extracting more electricity from the same amount of fuel to operate without combustion. It is virtually free of pollution and has a quieter operation because there are no moving mechanical parts (Stambouli & Traversa, 2002a).

The initial concept of fuel cells is attributed to the German physical-chemist Friedrich Wilhelm Ostwald in 1894. His idea was to modify the internal combustion engines, eliminating the intermediate stage of combustion and convert chemical energy into electrical energy in a single step. His devices project provided the direct oxidation of natural fuel and oxygen from the air, using the electrochemical mechanism. The device that would perform this direct conversion was called a fuel cell (Wand, 2006).

Ostwald's concepts marked the beginning of a great deal of research in the fuel cells field. Ostwald examined only the theoretical aspect of energy conversion in fuel cells, but completely ignored other practical aspects: the question of whether the electrochemical

reactions that involve natural fuels are feasible or not and how they can be efficient. The first experimental studies, conducted after the publication of Ostwald's document, indicated that it was very difficult to build devices for the direct electrochemical oxidation of natural fuels (Wand, 2006).

Ceramic fuel cells came up much later, initially with the discovery of the Nernst solid oxide electrolytes in 1899 [9]. Nearly forty years later, the first ceramic fuel cells began operating at 1000 °C, developed by Baur and Preis in 1937 (Farooque & Maru, 2001). Since 1945, three research groups (USA, Germany and the USSR) made studies on a few main types of generators by improving their technologies for industrial development. This work yielded the current concepts on fuel cells (Wand, 2006).

Nowadays, the development of fuel cells is being mainly driven by environmental reasons mentioned above. Over the last decades, advances in research made possible for a considerable improvement to happen, regarding the characteristics of the cells, in particular their stability and efficiency. Currently, it is possible to classify the fuel cells into two major groups, which differ by basic operational characteristics: the low-temperature and high temperature fuel cells.

1.1 Low-temperature fuel cells

The first large group of fuel cells, the low temperature ones (50 - 250 °C), is characterized by its more focused application on mobile devices and the automotive industry. Within the large group of low-temperature cells, there can also be a division, considering the type of electrolyte used. This classification results in three cell types: proton exchange membrane fuel cell (PEMFC), alkaline fuel cell (AFC); and phosphoric acid fuel cell (PAFC).

1.1.1 Proton exchange membrane fuel cell (PEMFC)

PEM fuel cell uses a solid polymer electrolyte, which is an excellent protonic conductor. In this electrolyte the ion exchange occurs between two porous electrodes. The operating temperature of the fuel cell type PEM is about 100 °C (Ellis et al., 2001).

The advantages of PEM fuel cell are its high charge density and its fast startup time, interesting features for automotive applications. The low temperature makes the technology competitive in the transportation sector and in commercial applications such as laptop computers, bicycles and mobile phones. The main disadvantages of PEM fuel cell are its low operating efficiency (40-45%) and the use of a noble catalyst such as platinum, whose CO intolerance ends up limiting the further popularization of this cell type (Farooque & Maru, 2001).

Two subcategories of PEM fuel cells are currently being widely studied, for allowing the use of other fuels other than hydrogen directly into the cell: direct methanol (DMFC) and direct ethanol (DEFC).

DMFC and DEFC fuel cells use a solid polymer electrolyte for ionic transport. However, they use, respectively, liquid methanol and ethanol as fuel instead of hydrogen. During chemical reactions, the fuel (methanol or ethanol) is directly oxidized in the anode. At the cathode, the reaction occurs with oxygen, producing electricity and water as a byproduct (Ellis et al., 2001; Garcia et al., 2004).

1.1.2 Alkaline fuel cell (AFC)

Initially, it was called Bacon cell, by virtue of its inventor Francis Thomas Bacon. It operates at low temperature around 100 °C and it is able to achieve 60-70% efficiency. It uses an aqueous solution of potassium hydroxide (KOH) as electrolyte solution. This fuel cell has quick startup speed, one of its great advantages. The main disadvantage is that it is very sensitive to CO_2 (Farooque & Maru, 2001). It needs an external system to remove CO_2 from the air. Furthermore, the use of a liquid electrolyte is also a disadvantage because it reduces the cell lifetime and makes the assembly handling and transport more difficult.

1.1.3 Phosphoric acid fuel cell (PAFC)

The phosphoric acid fuel cell (PAFC) operates at around 175-200 °C. This range of operating temperature is almost twice as high as the PEM's. It uses phosphoric acid as electrolyte. Unlike PEMFC and AFC, the PAFC is very tolerant to impurities in reforming hydrocarbons. The chemical reaction involved in this type of fuel cell is the same as PEMFC, where hydrogen is used as fuel input, however PAFC is more tolerant to CO_2 (Farooque & Maru, 2001). Cogeneration is also possible due to its relatively high operating temperature. The disadvantage of the PAFC is the same as the PEM's, its cost also increases due to the use of platinum as a catalyst (O'Sullivan, 1999).

1.2 High temperature fuel cells

The second major group of fuel cells, the high temperature ones (650 - 1000 °C) has as its main feature the high efficiency, since the high operating temperature facilitates the reactions. One application of this type of fuel cell is stationary generation, such as primary or secondary source of energy. Two cell types in this group are molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC).

1.2.1 Molten carbonate fuel cell (MCFC)

The molten carbonate fuel cell (MCFC) operates at high temperature, which is about 600-700 °C. It consists of two porous conductive electrodes in contact with an electrolyte of molten carbonate. This type of cell allows the internal reform. The main advantage of the MCFC is its high efficiency (50-60%) without external reformer and metal catalyst, due to the high operating temperature (Farooque & Maru, 2001). This cell is intolerant to sulfur and its launching is slow, these are its main disadvantages.

1.2.2 Solid oxide fuel cell (SOFC)

The solid oxide fuel cell (SOFC) is the cell that operates at the highest temperatures (800-1000 °C). It uses a solid electrolyte, which consists of a dense ceramic material with high ionic conductivity. In this cell, oxygen ion is transported through the electrolyte and, in the interface with the anode, it combines with hydrogen to create water and energy. The main advantages of the SOFC are that it produces electricity with high efficiency of 50-60% and does not require an external reformer to extract hydrogen from fuel due to its ability to internal reform. The waste heat can be recycled to produce additional electricity in the operation of cogeneration. The high temperature, which provides satisfactory characteristics

in the cell as already mentioned, is also responsible for its major disadvantages, such as the problems of material selection, high heat detritions and the impossibility of using metallic materials, which cost much less than the ceramic materials currently used (Aruna & Rajam, 2008; Farooque & Maru, 2001; Srivastava et al., 1997).

1.3 Evolution of SOFC

The studies on solid oxide fuel cells have promoted considerable improvements on their characteristics and properties. Several layouts were developed to improve the characteristics of SOFC, considering the current needs and costs of production and efficiency.

1.3.1 Tubular layout

The solid oxide fuel cell is highly influenced by the temperature variation during operation, constantly suffering from thermal stress, which requires excellent compatibility between the thermal expansion coefficients of the cell components. The cylindrical shape of tubular SOFC contributes significantly to minimize the difference in the coefficients of thermal expansion, thus avoiding the formation of cracks and delamination. This model also makes unnecessary the use of sealant gases. On the other hand, the efficiency is impaired, since the path made by the electric current is increased, causing ohmic losses (Minh, 1993).

1.3.2 Planar layout

This design consists of flat electrodes and electrolyte, separated by thin interconnects. The components can be manufactured separately, giving the production simplicity. It has higher energy density than the tubular. A disadvantage is the long time needed for heating and cooling of the cell, used to prevent the formation of cracks (Minh, 1993).

Inside the planar design of SOFC cells, the development of new materials and techniques of production allowed an evolution of the configurations of planar cells.

The first generation of SOFC fuel cells (1G-SOFC) operated at temperatures of around 1000 °C. The system consisted of electrolyte support and the mechanical stability of the cell was given by the thickness of the electrolyte. In this design the anode and cathode were quite thin (around 50 μm), while the electrolyte had thickness of 100 μm to 200 μm. However, the operating temperature of the cell was a limiting factor in popularizing this type of energy source, which led to the development of new designs for the cell (Wang, 2004).

At high temperature, the thickness of the electrolyte around 200 μm did not provide a problem in the ionic conductivity. However, the reduction of cell operating temperature to 700 °C - 800 °C would result in a drastic reduction of the electrolyte conductivity, so, the second generation of planar SOFC (2G-SOFC) was developed aiming to reduce the electrolyte thickness. The mechanical stability of the cell can no longer be granted by the electrolyte, which now is less than 20 μm. For that, the second-generation cells are anode support type, where the anode is responsible for mechanical stability, with thickness between 300 μm and 1500 μm. In this generation, the cathode thickness was of 50 μm (Wang, 2004).

However, the costs of the cell are directly related to the costs of obtaining and producing ceramic materials present in their components, and an anode or cathode with very high thickness results in a substantial increase in production costs. This motivation led to the

development of third generation SOFC (3G-SOFC) interconnect support type, allowing a reduction in the ceramic components thickness, accompanied by a reduction in operating temperature of the cell (800 °C) and the use of metallic interconnects. In this design, the electrolyte thickness has less than 20 μm and both, anode and cathode thickness, has about 50 μm (Wang, 2004). Figure 1 shows a schematic configuration of planar SOFCs.
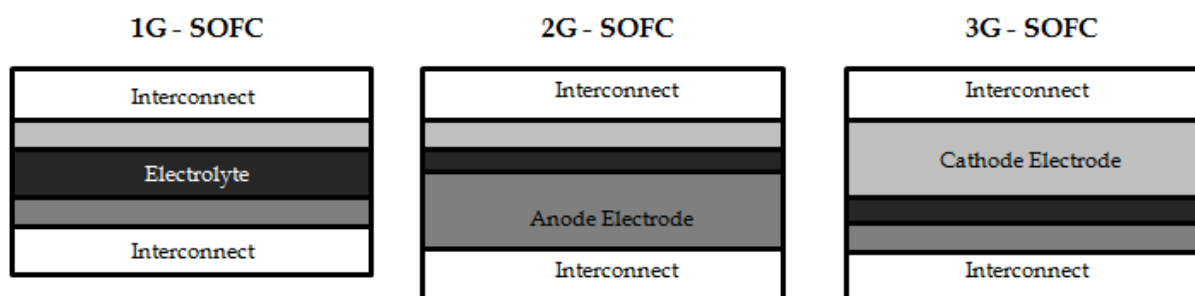

Fig. 1. Representation of the configuration for the three-generations of planar SOFCs.

1.4 Components of SOFC

1.4.1 Anode

The anode of a fuel cell is the interface between the fuel and electrolyte. The main functions of the anode are:

- Provide sites for electrochemical reactions of combustible gas catalytic oxidation with ions from the electrolyte.
- Allow the diffusion of fuel gas for the reactive sites of the electrode/electrolyte interface and the removal of byproducts.
- Transport of generated electrons to the interconnect (external circuit).

The anode material must possess, under the operating conditions of the fuel cell: good physical and chemical stability, chemical and structural compatibility with the electrolyte and interconnect, high ionic and electronic conductivity and catalytic activity for fuel oxidation (Ralph et al., 2001). The thermal stability is an important aspect to maintain the structural integrity throughout the temperature variations at which this component is subjected.

In general, the performance of the anode is defined by its electrical and electrochemical properties and therefore has a strong dependence on its microstructure. Thus, the control parameters, such as composition, size and distribution of particles and pores, are very important for optimizing the performance of the anode material of a solid oxide fuel cell.

Ceramic-metal composites, typically Ni-based, have been commonly used. Among them, the NiO-YSZ composite is the material of conventional fuel cells. Ni is also used because it has good electrical, mechanical and catalytic properties (Ralph et al., 2001). More recently, mixed conductors based on ceria (NiO-GDC) and transition metal perovskites (such as Fe, Mn, Cr and Ti) are being studied as potential candidates for anode materials for solid oxide fuel cells. However, to date, these materials do not present, in reducing atmospheres, values of electronic conductivity high enough for high performance fuel cell (Gong et al., 2010). The oxides of transition metals can have different oxidation states that can induce electron

transport, and usually increase the catalytic activity. Some compositions can be highlighted, such as: $Zr_{1-x-y}Ti_xY_yO_2$ (Tao & Irvine, 2002), $La_{1-x}Sr_xA_{1-y}M_yO_3$ (A: Cr ou Fe; M: Ru, Cr ou Mn) (Sauvet & Fouletier, 2001), $Sr_{1-x}Y_xTiO_3$ (Hui & Petric, 2001), e $La_{1-x}Sr_xTiO_3$ (Canales-Vázquez et al., 2003).

1.4.2 Cathode

The cathode of a fuel cell is the interface between air (or oxygen) and the electrolyte. Its main functions are to catalyze the reaction of oxygen reduction and to transport the generated electrons to the interconnect (external circuit).

In the same way of all the materials used in solid oxide fuel cells, the cathode must present certain general characteristics:

* Low cost and ease of fabrication.
* Minor differences between the thermal expansion coefficients of various components in the cell.
* Phase and microstructure stability during the operation.
* Chemical stability.
* High electrical conductivity, both electronic and ionic
* Porous microstructure during the entire operation of the cell
* High catalytic activity for oxygen reduction and stability in highly oxidizing atmospheres.

The materials, perovskite-type ABO_3, commonly used as cathodes in fuel cells are solid oxide ceramics based on lanthanum manganite ($LaMnO_3$) substituting A for Sr ions. This material fills most of the requirements for its use as cathode for ceramic fuel cells operating at temperatures around 1000 °C. The ionic conductivity of materials based on $LaMnO_3$ is significantly smaller than the ionic conductivity of YSZ electrolytes, but the ionic conductivity increases significantly substituting Mn for Co. The diffusion coefficients of oxygen ions in lanthanum cobaltite can reach 4-6 orders of magnitude higher when compared to those of lanthanum manganites with similar doping (Carter, 1992). Other materials have been used as cathode in SOFC, such as: Lanthanum strontium ferrite (LSF), (LaSr)(Fe)O_3, Lanthanum strontium cobaltite (LSC), (LaSr)CoO$_3$, Lanthanum strontium cobaltite ferrite (LSCF), (LaSr)(CoFe)O_3, Lanthanum strontium manganite ferrite (LSMF), (LaSr)(MnFe)O_3, Samarium strontium cobaltite (SSC), (SmSr)CoO$_3$, Lanthanum calcium cobaltite ferrite (LCCF), (LaCa)(CoFe)O_3, Praseodymium strontium manganite (PSM), (PrSr)MnO$_3$, Praseodymium strontium manganite ferrite (PSMF), (PrSr)(MnFe)O_3 (Stambouli & Traversa, 2002b).

1.4.3 Electrolyte

The design of fuel cells with solid oxide electrolyte must be based on the concept of oxygen ion conduction through the electrolyte, with ions O^{2-} migrating from the cathode to the anode, where they react with the fuel (H_2, CO, etc..) generating an electrical current.

The materials that have been studied the most are: yttria stabilized zirconia, doped ceria with gadolinium and lanthanum gallate doped with strontium and magnesium. The solid oxide fuel cells can, in principle, operate in a wide temperature range between 500 °C and

1000 °C. Thus, they can be divided into two types: operating at high temperatures (> 750 °C) and intermediate temperatures (500 °C to 750 °C). One of the determinant factors for the operating temperature is the characteristic of the solid electrolyte. The ohmic losses associated with the electrolyte are important for the cell performance. In order to reduce the operating temperature of SOFC, aiming the use of more conventional steel alloys as interconnects at temperatures around 700 °C (Horita et al., 2008; Perednis & Gauckler, 2004), it is necessary to employ electrolytes with high oxygen ionic conductivity at low temperatures.

YSZ is so far the most widely used solid electrolyte for application in high temperature SOFC. For many years, the zirconium oxide is already known as a conductor of oxygen ions.

The yttria addition to the zirconia-yttria solid solution has two functions: to stabilize the cubic structure type fluorite and to form oxygen vacancies in concentrations proportional to the yttria content. These vacancies are responsible for high ionic conductivity. Yttria stabilized zirconia is a suitable ionic conductor at temperatures above 800 °C, since thin dense membranes (less than 20 µm) can be manufactured. These membranes should be free of impurities. The stabilized zirconia is chemically inert to most reactive gases and electrode materials.

In view of the limitations encountered in using other types of ceramic conductors than yttria stabilized zirconia, its efficiency at low temperatures had to be improved. To reduce the operating temperature of the cell without affecting the efficiency of oxygen ion conduction, the electrolyte has to be as thin as possible in order to compensate the increase in ohmic losses (Huijsmans, 2001). Other advantages of fuel cells with thin electrolytes are reduction in material costs and improvement in the characteristics of the cells (Perednis & Gauckler, 2004). Therefore, the yttria stabilized zirconia is still a material with great prospects in the application as electrolyte in solid oxide fuel cells. Research about this type of material is aimed to improve its characteristics in order to adapt the needs of current applications.

1.5 Techniques to obtain SOFC materials

The methods employed in the deposition of thin films of oxides can be divided into two major groups based on the nature of the deposition processes. Physical methods of deposition: physical vapor deposition (PVD) (Kueir-Weei et al., 1997), ion beam (Xiaodong et al., 2008) and sputtering (Haiqian et al., 2010). The chemical methods of deposition, which can be subdivided as to the nature of the precursor: gas phase and solution. The gas phase methods: chemical vapor deposition (CVD) (Bryant, 1977) and atomic layer epitaxy (ALE) (Suntola, 1992). The solution methods: spray pyrolysis (Chamberlin & Skarman, 1966), sol-gel (Brinker et al., 1990) and electrodeposition.

The table 1 shows de main advantages and disadvantages of some technique that can used to obtain SOFC materials.

The technique of spray pyrolysis can be used to obtain both, dense or porous oxide films, and to produce ceramic coatings and powders. Compared to other deposition techniques, spray pyrolysis is a simple method for operational control. It is also cost-effective, especially regarding the cost of system implementation. Furthermore, deposition in multi-layers can be easily obtained by this versatile technique.

Technique	Advantage	Disadvantage
CVD	Applicable to ceramic coatings	Thin, non-uniform coatings, high cost
Screen printing	Simple	Non-uniform, porous coating
Spray pyrolysis	Simple, applicable to ceramic coatings, low cost	Many experimental variables
Sol-gel	Simple, applicable to ceramic coatings	Thin, non-uniform coatings
Electrodeposition	Simple, effective for complex shapes	Complex for ceramic materials

Table 1. Advantages and disadvantages of some techniques used to obtain SOFC materials.

1.5.1 Spray pyrolysis

A typical setup for spray pyrolysis consists of an atomizer, the precursor solution, the heated substrate and a temperature controller. Three types of atomizers are commonly used in spray pyrolysis: compressed air (the solution is exposed to a beam of air) (Balkenende et al., 1996); ultrasound (short wavelengths are produced by ultrasonic frequencies, generating a very fine spray) (Arya & Hintermann, 1990); electrostatic (the solution is exposed to a high electric field) (Chen et al., 1996).

Films prepared by spray pyrolysis have been used in several devices, such as solar cells, sensors, anti-reflective coatings, thermal barriers, solid oxide fuel cells, among others.

The deposition of thin films via spray pyrolysis involves spraying a metallic salt solution on a heated substrate. The solution droplets reach the substrate surface, where solvent evaporation and the decomposition of the metal salt occurs, forming a film. The film morphology and thickness depend on the volume of solution sprayed and the substrate temperature. The film formed is usually a metal salt, which is converted to oxide in the heated substrate.

Many processes occur sequentially or simultaneously during the formation of a thin film by spray pyrolysis: atomization of the solution, transport and evaporation of solution drops, solution spread on the substrate, evaporation of the solvent and, finally, drying and decomposition of the precursor salt. Understanding these processes helps to improve the quality of the films obtained, facilitating the production scale and reproducibility of the process.

The initial parameter in the preparation of a film with certain desired characteristics, using the technique of spray pyrolysis, is the definition of the precursor solution to be used. This solution should provide the ions, needed to form the desired film, and should contain a solvent, with adequate evaporation rate and stability in the process conditions.

In the aerosol, the drops of solution are transported and eventually evaporate. The gravitational, electrical or thermophoretic forces, have influence on the trajectory of droplets and their evaporation, so the modeling of film growth should be taken into account.

When the formation of dense films is wanted, it is important that the maximum amount of drops reaches the substrate without the formation of particles along the path. Sears et al.

investigated the mechanism of SnO_2 film growth (Sears & Gee, 1988). In case of excessively rapid evaporation of the solvent along the way, the droplet size decreases and precipitates precursor salt on the edges of the drop, causing the deposition of precipitates on the substrate surface. This phenomenon is extremely deleterious to obtain dense and homogeneous films, since the particles formed in the atomizer-substrate path add to the substrate surface, forming a porous crust (Perednis, 2003).

On the other hand, if the drops are sprayed against the substrate with sufficiently high strength, spread lightly, maintain an evaporation rate equivalent to the solute precipitation rate, the solute nucleates and precipitates homogeneously, creating a dense and continuous film (Yu & Liao, 1998).

A model of the possible transport situations of aerosol from the atomizer, toward the heated substrate can be seen in Figure 2. In zone I, the droplet is too large, has a very slow solvent evaporation rate and results in the formation of a brittle precipitate. In the second case, the drops have size and strength suitable for spraying, forming homogeneously aggregates of precipitates (zone II). And finally, in zone III, the drops are too small and not strong enough to reach the substrate, causing particles to appear before reaching the substrate.
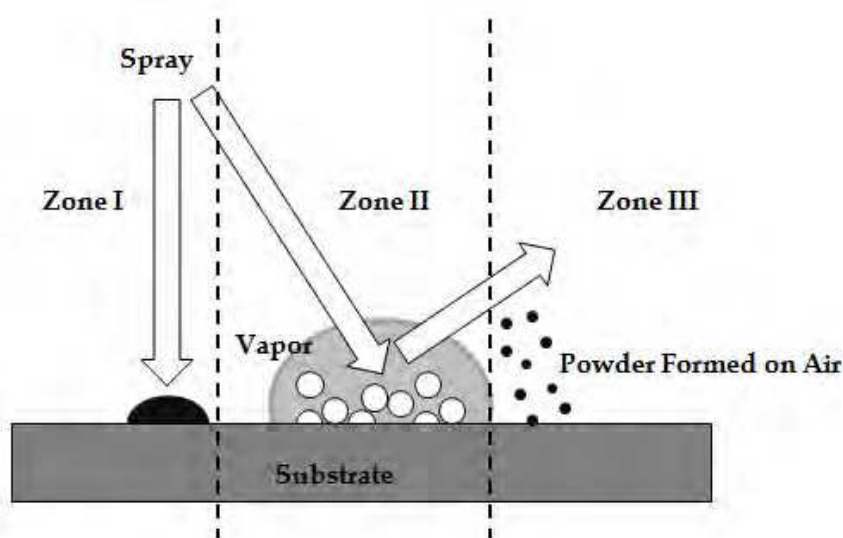
Fig. 2. Aerosol transport model.

The substrate temperature can be considered the most important factor to determine the solvent evaporation rate. It is directly linked to the time the solvent takes to spread over the surface of the substrate and the speed at which it evaporates after being spread. In addition, the substrate temperature should be high enough so that the salt decomposition reactions occur, in order to form the desired final material.

It is known that low substrate temperatures provide an excellent scattering of the solution, however, the film layer that is formed is very rich in solvent, taking too much time to evaporate. After stopping the solution spraying, the film is still wet and the local rise in temperature causes the solvent to evaporate, diminishing the volume and contributing to the formation of tension in the film. The strong adhesion between film and substrate prevents free contraction of the film, promoting the formation of cracks (Neagu et al., 1981).

However, if the substrate temperature is high, it will reduce the time of solvent evaporation to a point when the solvent partially evaporates before touching the substrate, inhibiting the spread. In cases where the temperature is too high, the droplets of solution not even touch the substrate, all the solvent is evaporated on the way between the atomizer and the surface and only particles are deposited on the substrate (Perednis & Gauckler, 2004).

The choice of an intermediate temperature is necessary to obtain a film with the desired characteristics. This should consider the solvent used, so it evaporates after a light scattering of the solution on the substrate.

1.6 Research directions

In recent years, research has been aimed at further reducing the operating temperature of the cell, leading to the development of a new class of planar SOFC, the intermediate temperature (IT-SOFC). This configuration provides an even greater reduction in operation temperature, allowing a large-scale use of metal interconnects. However, the ionic conductivity of the electrolyte is greatly affected by reducing the temperature. In this context, there are two ways to develop electrolytes for IT-SOFC: by changing the electrolyte to a material that has a high conductivity; or by reducing of the electrolyte thickness. In IT-SOFC cells, the electrolyte thickness should be as thin as possible (less than 10 μm has been suggested). In this case, the cell can operate at temperatures between 600 °C and 800 °C (Cooper et al., 2008).

In recent years, research has been aimed at further reducing the operating temperature of the cell, leading to the development of a new class of planar SOFC, the intermediate temperature (IT-SOFC). This configuration provides an even greater reduction in operation temperature, allowing a large-scale use of metal interconnects. However, the ionic conductivity of the electrolyte is greatly affected by reducing the temperature. In this context, there are two ways to develop electrolytes for IT-SOFC: by changing the electrolyte to a material that has a high conductivity; or by reducing the electrolyte thickness. In IT-SOFC cells, the electrolyte thickness should be as thin as possible (less than 10 μm has been suggested). In this case, the cell can operate at temperatures between 600 °C and 800 °C.

For the case of electrolyte change, materials with better ionic conductivity than YSZ have been studied to replace it. LSGM has been successful when applied with a metallic Ni anode, presenting ionic conductivity in temperatures around 400 °C (Sasaki et al., 2008; Tuker, 2010). The problem with such material is its low chemical stability. Another exhaustly studied material for SOFC electrolyte is gadolinium-doped ceria (CGO). This material has better ionic conductivity than YSZ and can be used in lower temperatures. However, at 600 °C the Ce reduction occurs. This reduction confers electric conduction to the material and the cell can suffer a short circuit (Tuker, 2010; Yuan et al., 2010).

The greatest challenge nowadays is to reach fuel cells operating around 700 °C without efficiency losses. The operation temperature can be lowered when the electrolyte thickness is reduced and the densification optimized. Several researches aim the obtaining of thin and dense electrolytes (Gaudon et al., 2006).

In the present study, some results about the elaboration of the YSZ thin film by spray pyrolysis process will be presented.

2. Materials and methods

The spray pyrolysis setup consisted mainly of the following parts: a spraying unit, a liquid feeding unit, and a temperature control unit (Figure 3). The spray unit consisted of an airbrush (Campbell Hausfeld) using an air blast atomizer. The liquid feeding unit is the precursor solution, constituted by yttrium chloride ($YCl_3.6H_2O$) (Aldrich Chemicals) and zirconium acetylacetonate ($Zr(C_6H_7O_2)_4$) (Aldrich Chemicals) dissolved in three different solvents: (1) mixture of ethanol (C_2H_5OH) (FMaia) and propylene glycol ($C_3H_8O_2$) (Proton) (1:1 vol.%); (2) mixture of ethanol and 2-methoxy, 1-propanol ($C_4H_{10}O_2$) (Aldrich Chemicals) (1:1 vol.%); (3) mixture of ethanol and diethylene glycol monobutyl ether ($C_8H_{18}O_3$) (Aldrich Chemicals) (1:1 vol.%). The Table 2 shows the boiling temperatures of any individual solvents used in this work.

Fig. 3. Spray pyrolysis experimental apparatus.

Solvent	Boiling Point [°C]
ethanol	78.4
propylene glycol	188.2
2-methoxy, 1-propanol	120.0
diethylene glycol monobutyl ether	230.4

Table 2. Boiling temperatures of the solvents used.

The solutions were prepared according to the stoichiometry required to the films $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ (Perednis & Gauckler, 2004) and adopting a final concentration of salts in solution of 0.1 mol.L^{-1}. The precursor solution was maintained under stirring and heating at 50 °C in a hotplate stirrer (Fisaton), in order to obtain the complete dissolution of the salts and decrease the heat loss of the substrate. Finally, the temperature control unit consisted in a hotplate, used for heating the substrate. A thermostat controlled the hotplate temperature and the substrate temperature was monitored by an infrared pyrometer. The precursor solution was sprayed on the heated LSM porous substrate, in order to obtain the YSZ films.

The substrate temperature is determining in the morphology of films obtained, since it is directly related to the solvent evaporation rate, and a quick evaporation of the solvent promotes the formation of particles instead of forming a continuous film. On the other hand, the slow evaporation of the solvent, promotes crack formation in the film. Previous studies were made to determine the optimum temperature to obtain continuous films. For this reason, in this chapter, a single temperature was studied, 350 °C.

Three other important parameters influence in the solvent evaporation rate and in the attainment of dense and continuous films: solution flow rate, nozzle distance and air pressure,. In this study, these parameters were kept constant, and their values were, respectively, 35 mL.h^{-1}, 250 mm and 3 kgf.cm^{-2}.

The YSZ films are amorphous, after deposition, and a heat treatment was required in order to stabilize the zirconia cubic phase. This heat treatment was performed at 700 °C for two hours in a furnace with a constant heating rate of 2 °C.min^{-1} and slow cooling.

Two protocols were used for the film deposition: one-step deposition and multi-layer deposition. The first protocol consists in a deposition of 50 mL of precursor solution followed by heat treatment and the other protocol consists in a deposition of 150 mL of precursor solution in three sequential steps with intermediate heat treatment after each deposition.

The microstructure and the morphology of the films were evaluated by Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM).

3. Results and discussion

3.1 Microstructural characterization

3.1.1 X-ray diffraction (XRD)

The spectrum of X-ray diffraction (Figure 4) shows that after the deposition, the film is amorphous.
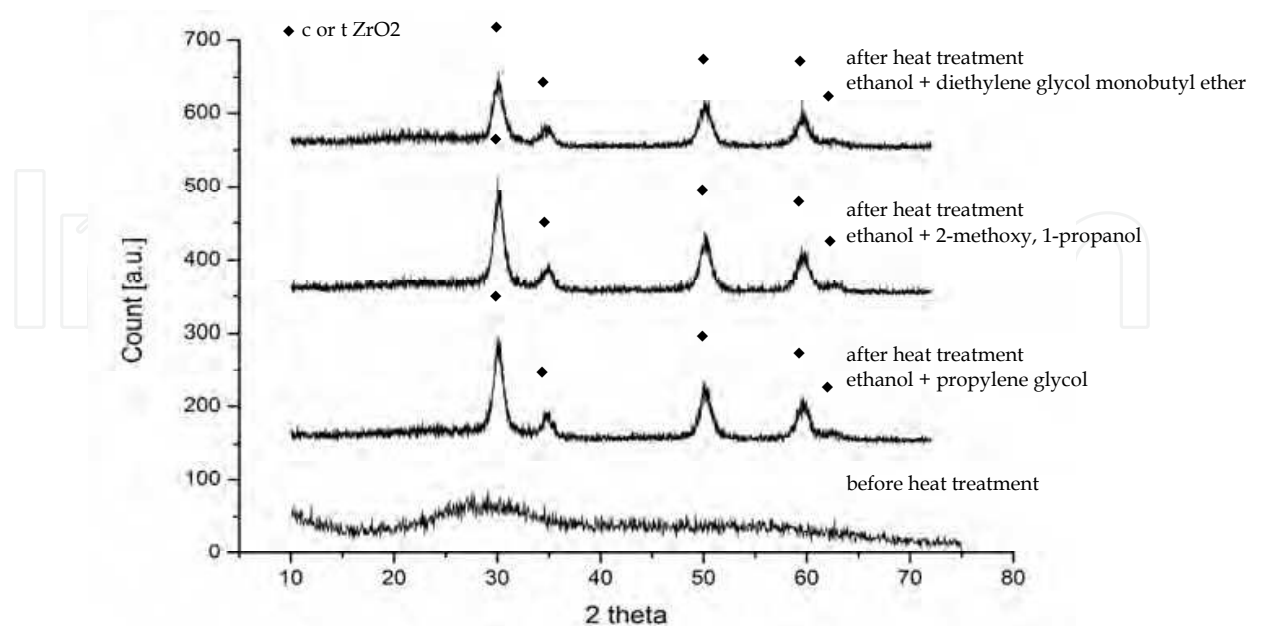
Fig. 4. XRD spectrum of YSZ obtained from different precursor solutions before and after heat treatment at 700 °C for 2 hours.

However, after the heat treatment at 700 °C for 2 hours, the crystallization of zirconia was observed for all the solutions tested. There was no influence of the solvent used in the stabilization of the zirconia phase. The overlapping of the tetragonal and cubic zirconia peaks impedes the determination of the predominant stabilized phase (Wattnasiriwech et al., 2006). Given the importance of determining the stable phase, other techniques can be used to complement the analysis of YSZ X-ray diffraction. In this work Fourier Transform Infrared Spectroscopy (FT-IR) was used to determinate the zirconia phase stabilized.

3.1.2 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectrum (Figure 5) shows a very pronounced peak around 471 cm^{-1} (zone IV). Comparing it to FT-IR spectra for cubic zirconia, presented in the literature (Khollam et al., 2001), it is possible to see the presence of vibrational frequencies resulting from metal-oxygen bonds characteristic of this phase around 471 cm^{-1}, revealing that the heat treatment at 700 °C allowed the stabilization of the zirconia cubic phase for the films prepared. The band located at 3455 cm^{-1} (zone I) can be attributed to bonds O - H, possibly due to the presence of solvent excess adsorbed in the film. The bands presented around 2330 cm^{-1} (zone II) correspond to adsorbed atmospheric CO_2, according to (Andrade et al., 2006). In the region from 1630 to 1619 cm^{-1} (zone III), the bands correspond to asymmetric and symmetric stretch of COO-group (Farhikhte, 2010).
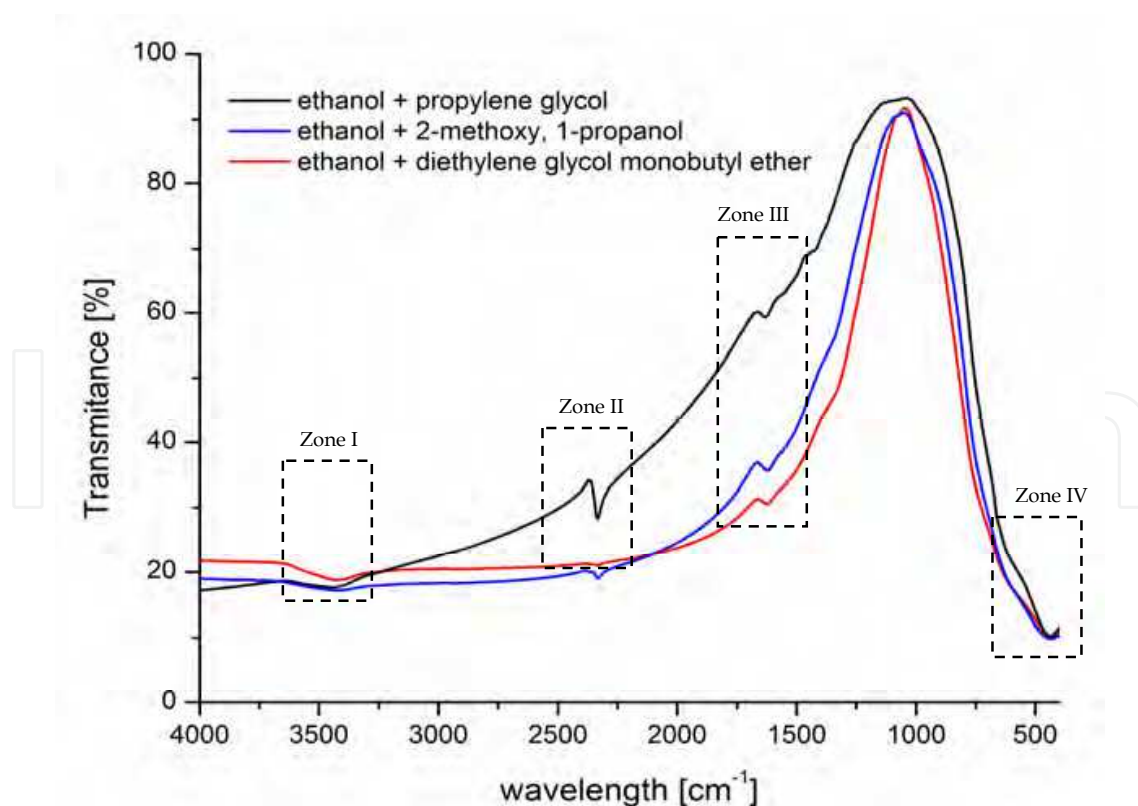
Fig. 5. FT-IR spectrum Of YSZ obtained from different precursor solutions after heat treatment at 700 °C for 2 hours.

3.2 Morphology characterization

3.2.1 One-step deposition (influence of solvent)

Variations of the solvent used in the precursor solution cause changes in the solution characteristics. A solvent mixture that has, for example, a lower boiling point, leads to a faster evaporation of the solvent for the same temperature. This stage of the study aimed to observe the morphological changes associated to the use of different solvents for the same temperature.

Figure 6 shows the film obtained at 350 °C, using ethanol and propylene glycol as solvent in the precursor solution. The morphology obtained showed a large amount of cracked plates. Locally, the plates are fairly homogeneous, with little porosity, as evidenced in detail showed in Figure 6b. This morphology may be associated to the high viscosity of the solvent, which hinders the spread of the solution on the substrate surface, resulting in a thicker solution film rich in solvent. When the solvent evaporates, the cohesion and adhesion to the substrate throughout the film generate a lot of residual stresses, causing the oxide film to crack.
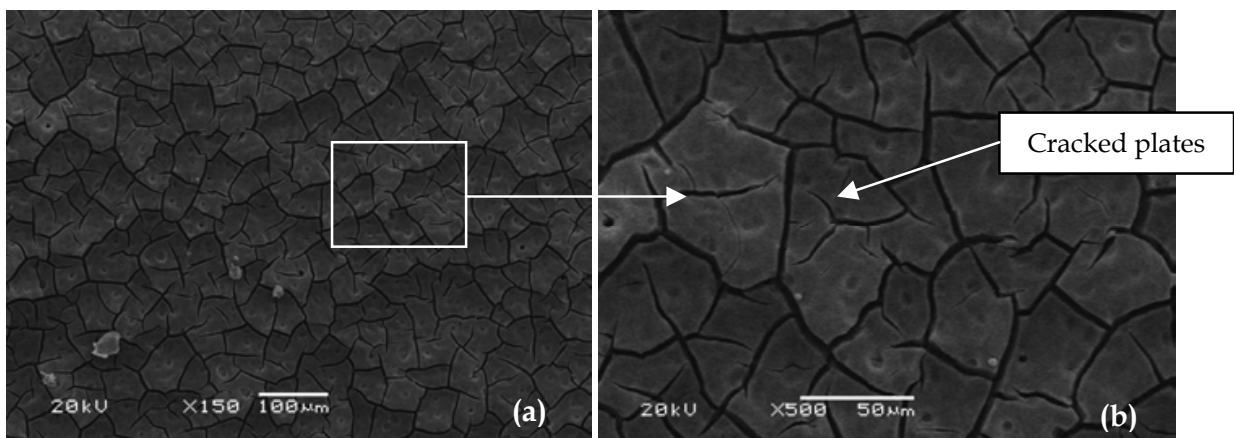
Fig. 6. (a) SEM image of the film obtained from ethanol and propylene glycol on the substrate at 350 °C, without heat treatment; (b) magnification of (a).

The films deposited from ethanol and propylene glycol solution presented clefts (Figure 6) and after heat treatment, the cracks increased, not only in number but also in intensity (Figure 7). The plates, which were well bonded to the surface, suffered a major influence of the contraction during the zirconia crystallization, contributing to the increase in cracking and detachment of the film as shown in Figure 7. This mechanism has been proposed by (Φstergård, 1995).

Depositions from the solution of ethanol and 2-methoxy, 1-propanol showed, at first, the formation of an apparently continuous film instead of plaque formation. This can be seen in Figure 8a. However, as this solution has lower boiling point and greater fluidity, there is a very high scattering on the surface. This phenomenon and the rapid evaporation of the solvent after the scattering, lead to a cracked film.

It is also possible to observe the deposition of some precipitates distributed over the layer of the film (Figure 8). These are related to the evaporation during the transport of the droplets toward the substrate, forming YSZ powder that clings to the surface of the film.
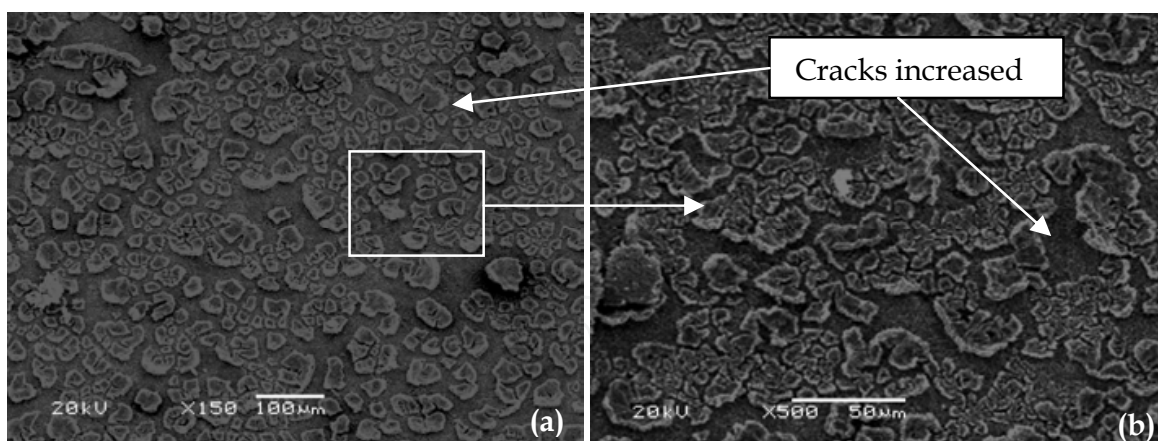
Fig. 7. (a) SEM image of the film obtained from ethanol and propylene glycol on the substrate at 350 °C, after heat treatment at 700 °C for 2 hours; (b) magnification of (a).

On the other hand, the film formed (Figure 8b), is not continuous and suggests the overlapping of non-homogeneous rough boards, which are formed during the rapid evaporation of the solvent. This type of morphology is undesirable to use in SOFC electrolyte, because it forms deep cracks and discontinuities.
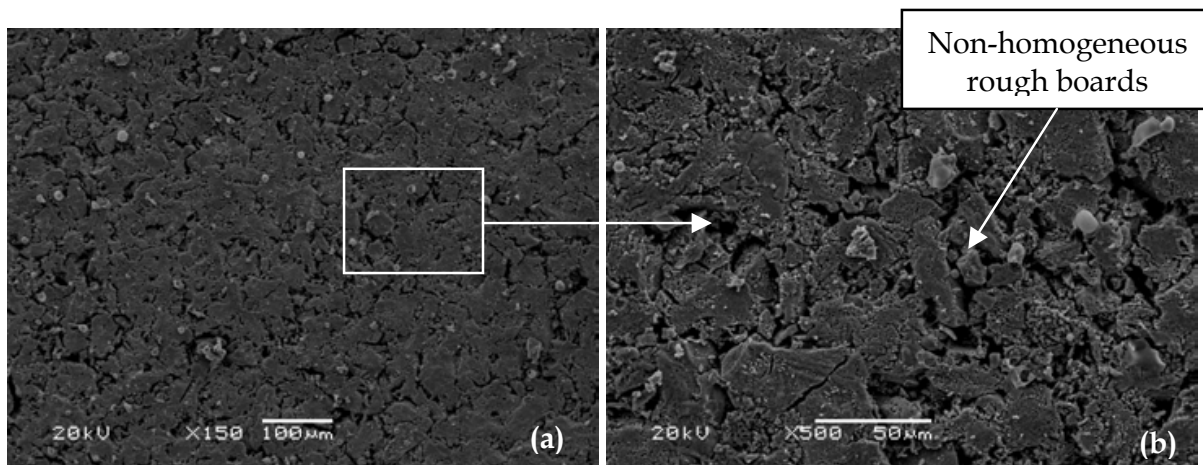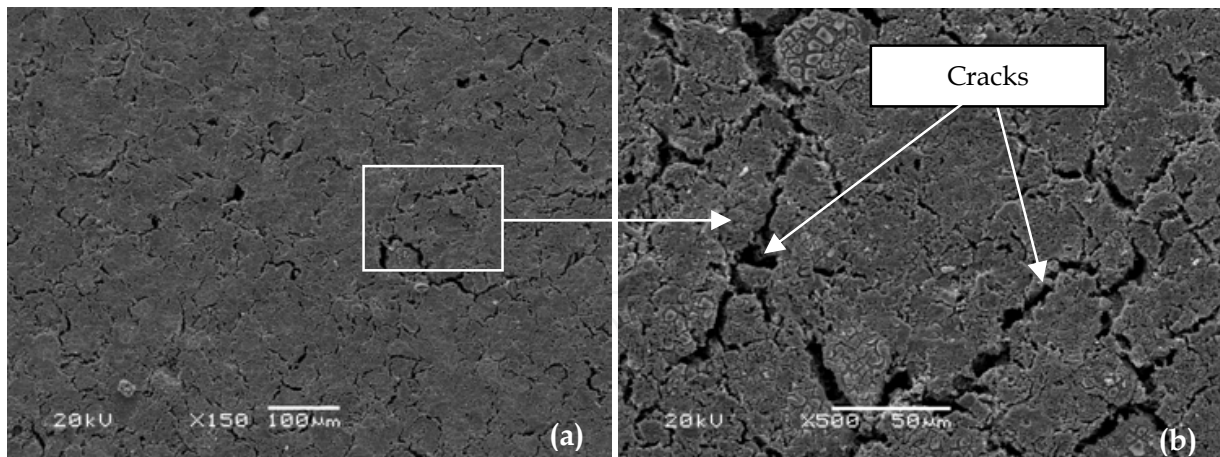

Fig. 8. (a) SEM image of the film obtained from ethanol and 2-methoxy, 1-propanol on the substrate at 350 °C, without heat treatment; (b) magnification of (a).

After heat treatment (Figure 9), there seems to be a softening of the cracks seen after the deposition, possibly related to the contraction during the zirconia crystallization. Which, in this case, tends to reduce overlapping plates, softening the final morphological structure. However, this effect is not enough to homogenize the surface, and the cracks are not completely eliminated (Figure 9b).

The films obtained from ethanol and diethylene glycol monobutyl ether showed a considerable reduction in the amount of cracks and discontinuities (Figure 10a). After a soft scattering of the solution onto the substrate surface, the solvent evaporates properly, thus reducing internal stresses in the film and reducing the number of cracks, making it more homogeneous (Neagu et al., 2006).

However, the magnification of the image (Figure 10b) revealed the presence of small cracks distributed throughout the film. These cracked regions jeopardize the homogeneity of the

Fig. 9. (a) SEM image of the film obtained from ethanol and 2-methoxy, 1-propanol on the substrate at 350 °C after heat treatment at 700 °C for 2 hours; (b) magnification of (a).

film and show that the use of this solvent alone is not enough for complete densification of the deposited layer.
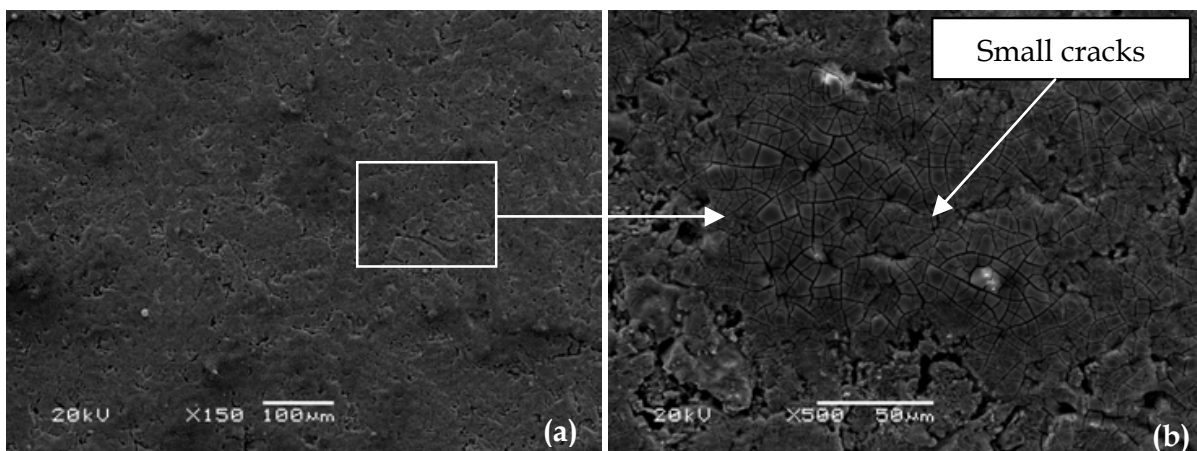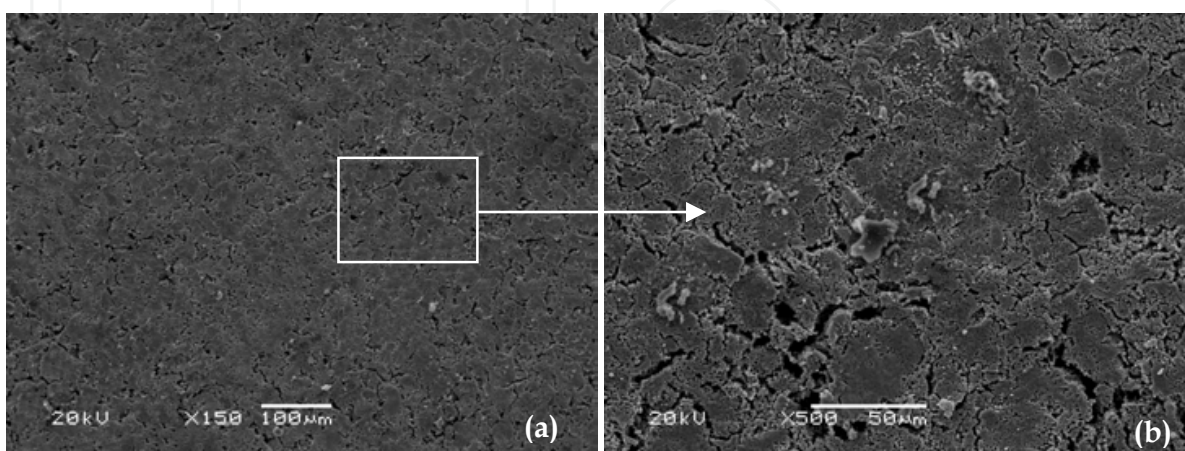

Fig. 10. (a) SEM image of the film obtained from ethanol and diethylene glycol monobutyl ether on the substrate at 350 °C, without heat treatment; (b) magnification of (a).

Fig. 11. (a) SEM image of the film obtained from ethanol and diethylene glycol monobutyl ether on the substrate at 350 °C, after heat treatment at 700 °C for 2 hours; (b) magnification of (a).

The films have undergone little morphological changes after heat treatment (Figure 11a). There was a slight increase of the cracks, which can be best shown in Figure 11b, that may be associated to the changes in the volume of the film during the crystallization of the zirconia cubic phase.

3.2.2 Multi-layer deposition

From the results obtained in depositions with different solvents, the solution (ethanol and diethylene glycol monobutyl ether) was chosen to use in the protocol of multi-layer depositions with intermediate heat treatment.

Figure 12 shows the film after the first layer deposition, where the surface is completely covered. After heat treatment (Figure 12b) there is a homogenization of the surface morphology, however, this homogenization is accompanied by the appearance of some discontinuities distributed throughout the film.
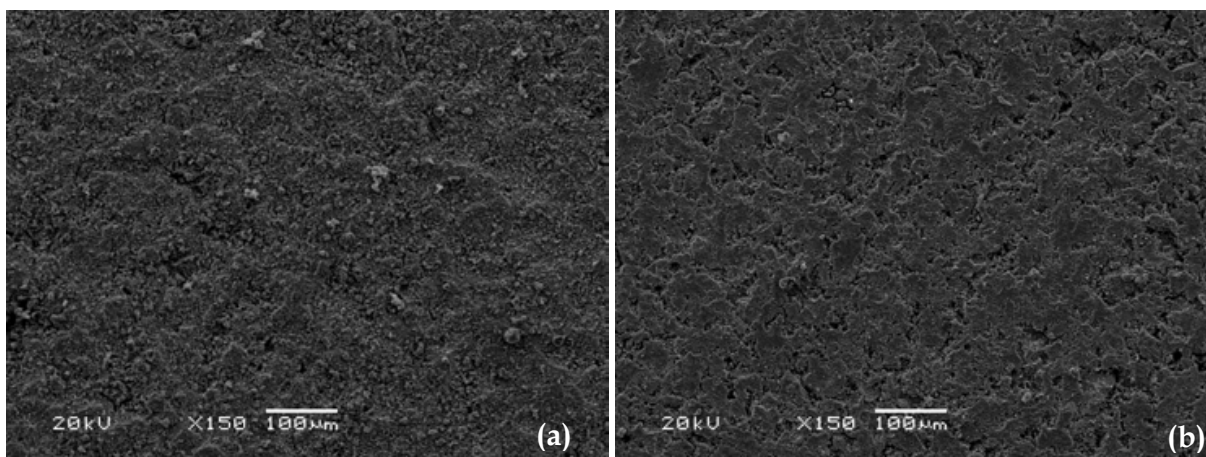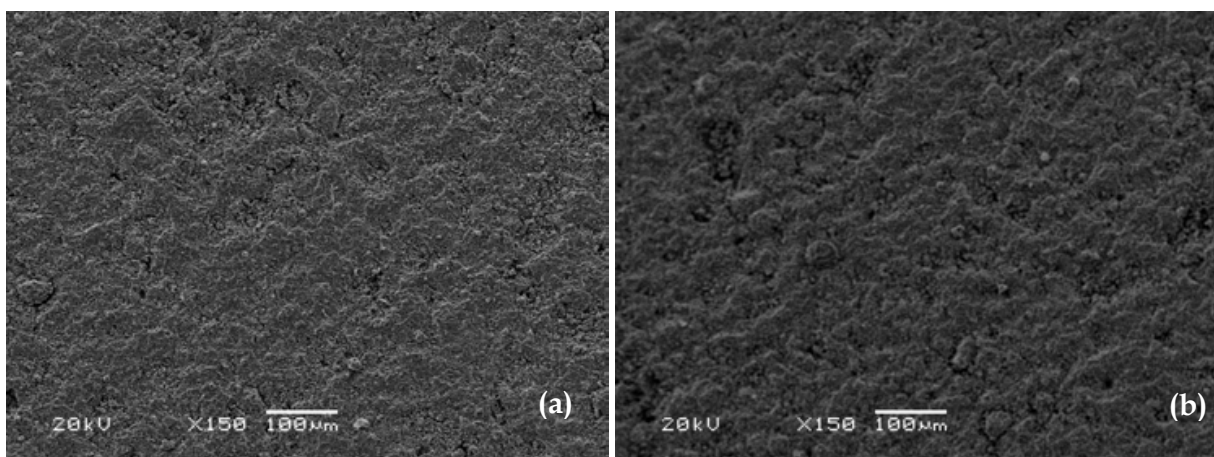

Fig. 12. SEM images of the film obtained from intermittent deposition at substrate temperature of 350 °C: (a) after the first deposition; (b) after the first heat treatment at 700 °C for 2 hours.
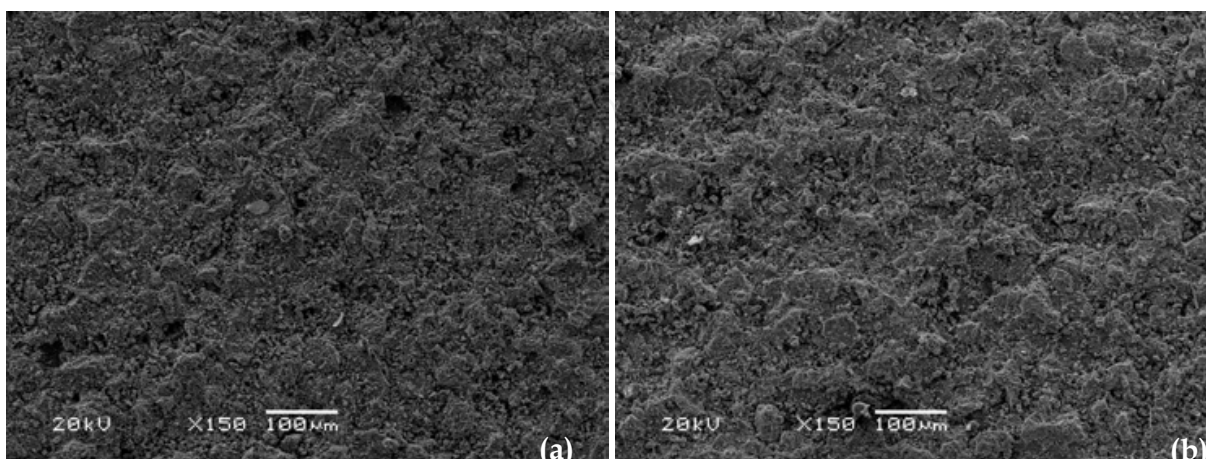
Fig. 13. SEM images of the film obtained from intermittent deposition at substrate temperature of 350 °C: (a) after the second deposition; (b) after the second heat treatment at 700 °C for 2 hours.

After the second layer deposition, the film covered most of these irregularities, achieving the aimed goal of the intermediate deposition protocol. However, the second and first layer overlapping, led to the formation of an even more irregular layer, both before (Figure 13a) and after heat treatment (Figure 13b).

The same behavior was observed after the last deposition. This layer apparently had some leveling effect on the film, slightly reducing the surface irregularities (Figure 14a). There were no significant morphological changes after the final heat treatment (Figure 14b). For the protocol of multi-layer depositions, with intermediate heat treatment, a crack-free film was obtained, but the surface presented a roughness increase.

Fig. 14. SEM images of the film obtained from intermittent deposition at substrate temperature of 350 °C: (a) after the final deposition; (b) after the final heat treatment at 700 °C for 2 hours.

4. Conclusions

Results showed that YSZ films can be obtained directly on porous LSM substrate by spray pyrolysis technique. A dense and homogeneous film can be obtained by multi-layers deposition with intermediate heat treatment.

The heat treatment at 700 °C allowed the stabilization of the zirconia cubic phase, which is the phase of interest for application as electrolyte in solid oxide fuel cells, as indicated by x-ray diffraction analysis and confirmed by the Fourier transform infrared spectroscopy analysis.

The type of solvent used influences in the morphology of the films obtained. Solvents that have very low boiling point lead to the uncontrolled evaporation of the solvent, forming a quite brittle film. The increase in the solvent boiling temperature helps to a proper evaporation, resulting in films with more satisfactory morphological characteristics. In all cases of one-layer deposition, heat treatment caused an increase of surface discontinuities, demonstrating its influence on the films morphology.

5. Acknowledgments

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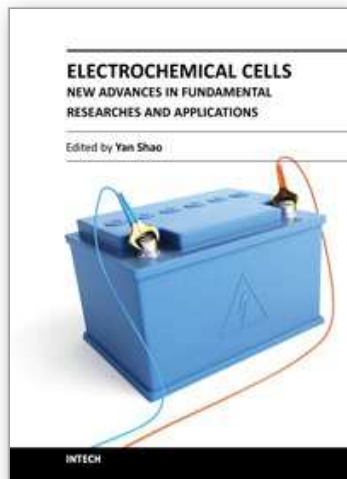
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