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# INNOVATIVE METHODS AND TECHNOLOGIES FOR ELABORATION OF SOFC CERAMIC MATERIALS
# (REVIEW)

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## ABSTRACT

*Nowadays, due to both of energetic and ecological demands, related to the sustainable development of the modern communities, the fuel cells have emerged as a new alternative energetic source. Their performance is predetermined by the structures, compositions, and properties of the used materials. On the other hand, the industrial employment of SOFC material depends on the method, and the conditions applied for its synthesis. The present work reviews the basic features of the sol-gel approach and the spray techniques for elaboration of SOFC materials and components.*

*Keywords: fuel cells, SOFC, sol gel processing, spray pyrolysis, spray freezing.*

## INTRODUCTION

The fuel cells, in their variety, as: Polymer-Electrolyte Membrane fuel cells (PEMFC), Alkaline Anion Exchange Membrane Fuel Cells, (AAEMFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel Cells (MCFC), and Solid Oxide Fuel Cells (SOFC) are an alternative source of electrical power [1]. When the fuel is not contaminated, the exhaust products of SOFC are composed of $CO_2$ and water vapors. The fuel cells produce thermal energy, together with the electric power [2, 3]. The simplest definition for a "fuel cell" is a device for conversion of chemical energy, by oxidation/reduction reactions, to electrical and thermal energy. The increased interest in SOFCs during the last years [4] is a result of their extremely high efficiency as co-generators of electricity and thermal energy from hydrogen or natural gas [3], their electro-catalytic abilities [5], and the potential to be used as sensors for combustible gases. Thus, when electric current is applied to SOFC from an external electric source, it could accelerate a given oxidation reduction process by up to $3.10^5$ times [5]. On the other hand, the molar concentration of a given combustible gas in a gas stream, is proportional to the electric current produced by the SOFC, predetermining its ability to be used as a gas sensor.

The research and development activities regarding SOFCs are directly related to elaboration and assessment of advanced ceramic materials with defined composition, granulometry, thickness and porosity. Additionally, the technologies for these materials should enable large scale (industrial) production.

In the above context, the aim of the present brief review is to describe three basic approaches for synthesis of ceramic materials used for SOFC components.

## REQUIREMENTS FOR SOFC MATERIALS

From a constructional point of view, the SOFC can be described as three layered ceramic bodies, composed by a cathode, a solid electrolyte and an anode, respectively, unless interlayer is necessary for interface improvement between the main layers. The negative effects of differences in the dilatation coefficients, or high temperature diffusion phenomena of the main layers can be avoided [6, 7]. Because of the fact that each

Table 1. Requirements for the layers.

| **Layer (Component)** | | |
|---|---|---|
| CATHODE | ELECTROLYTE | ANODE |
| **(i)** To ensure a stable layer with a sufficient porous microstructure parallel with good adhesion to the rest SOFC ceramic components;<br>**(ii)** To possess high electronic conductivity;<br>**(iii)** To possess an effective ionic (oxygen) conductivity;<br>**(iv)** High catalytic activity to $O_2$ dissociation and next reduction process;<br>**(v)** Compatibility and minimum reactivity with the electrolyte and the interconnection with which air electrode comes into contact. | **(i)** Electrochemical: high ionic conductivity;<br>**(ii)** Chemical: structural stabilization at high temperature, no reactivity to the other component materials and lack of instability to oxygen and fuel gas at high temperature treatment; lack of phase immiscibility is also necessary;<br>**(iii)** Thermal: thermal phase stability and low thermal expansion coefficient close to those values of the rest cell components. | **(i)** High stability at reduction atmosphere;<br>**(ii)** To have high temperature stability;<br>**(ii)** To be porous;<br>**(iii)** To possess high catalytic activity;<br>**(iv)** High electronic conductivity;<br>**(v)** High corrosion stability; |

layer has its own function, there are different requirements for each layer, as described elsewhere [1, 8]. The respective requirements are given in Table 1.

In summary, the properties of whatever complite SOFC – unit is the result of the combination among the properties of all composing elements (layers). Therefore, the performance of a SOFC is not limited only to its electrical characteristics, but also to its ability to keep them for large exploitation periods, at least for 3000 hours. So, the durability of a SOFC depends on the chemical, mechanical and structural resistivity of each composing layer, at working environment parameters, such as: temperature, pressure, composition and flow rate of the respective gaseous streams during the exploitation, as described elsewhere [9, 10].

Additional requirements arise for the technologies for synthesis of SOFC materials. These requirements originate from the demands for easy industrial production of SOFC materials, and the respective final products. From this point of view, the sol-gel approach, and the spray techniques should be the most appropriate methods for large scale SOFC industrial production. Besides, the sol-gel route has emerged as a versatile method for a large variety of new generations of materials [11], whereas the spray techniques enable quick production in an industrial scale, respectively [12]. Godbole et al. [13] point out a very important additional benefit of the spray pyrolysis techniques. According to them, the application of the spray pyrolysis is not related to the demand of expensive and sophisticated equipment unlike the Chemical of Physical Vapour Deposition methods, ion beam technologies, etc.

## APPLICATION OF THE SOL-GEL APPROACH FOR SOFC MATERIALS

Each technology which includes sol, or gel in an intermediated state could be considered a “sol-gel technology” [11, 14]. In that instance, the transitions of a colloidal systems (i.e.: sols), to solid polymeric matrices, with equally distributed liquid in their bulks (i.e.: gels) can be defined as sol-gel processes. If the sol-gel process involves the formation of an additional gaseous phase, due to evaporation of the liquid phase, or decomposition of some of its ingredients (i.e: nitrates, carbonates, etc. to the respective metallic oxides and gases), then the respective products, known as “xerogels” possess remarkable porosity. In the literature, there are various examples for successful synthesis of ceramic materials for SOFC via the sol-gel approach, and posterior calcinations. Suciu and co-workers [15] have developed synthesis of $Sc_2O_3$-$ZrO_2$ bulk materials, through xerogels and posterior calcinations. For that purpose, the sucrose and pectin xerogel has been formed by hot stirring of a mixture of $ScCl_3.6H_2O/ZrCl_4$ and additions of sucrose/pectin, as a polymerizing phase, at 90 °C for 5 hours. After removal of the water by drying, the obtained xerogel has been subjected to calcination at 650°C for 3 h. The obtained oxide powder has passed further isostatic pressing 1200 bars for 2 minutes, and subsequent sintering in order to obtain solid pellets. As a result, the authors report that using homogeneous nanocrystalline powders, obtained by the new modified sol-gel method, can be a feasible way to fabricate solid oxide fuel cells ceramics. New oxides of the general formula $Ln_{2/3''x}TiO_{3''3x/2}$ (Ln = La, Pr and Nd; 0.07

d" x d" 0.13) have been elaborated by Lepe et al. [16] using the Pechini method, followed by calcination. According to the authors, these new phases become candidates for solid oxide fuel cell (SOFC) anode materials. Synthesis of $LaSrFeO_4$, $La_2SrFe_2O_7$ and $LaSr_3Fe_3O_{10}$ has been carried out by Velinov and co. [17] through the nitrate-citrate method.

The oxides have been obtained from $HNO_3$, containing an aqueous precursor solution of $La_2O_3$, $Sr(NO_3)_2$ and $Fe(NO_3)_3.9H_2O$. The sol-gel procedure has been performed by the authors by addition of citric acid in molar ratio 3.3 : 1 in relation to metal ions at 200°C. After drying, the self-combustion of the dry residues gave powdered precursors. The posterior calcination was performed at different temperatures from 700 to 1100°C for 2 hours. The authors conclude that the calcination temperature has a significant role for the formation of the resulting oxide products.

Obtaining of gel intermediated products via polymerization of acrylamide is reported by Tarancσn and etc. [18]. By combustion of a priori prepared poyacrylamide gels, the authors succeeded to obtain an entire group of non-stoichiometric ceramic materials, such as: $Zr_{0.84}Y_{0.16}O_{1.92}$ (8YSZ), $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO), $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM), $La_2Mo_2O_9$, $La_{0.8}Sr_{0.2}CoO_{3-d}$ (LSC) and at last, $La_{0.8}Sr_{0.2}FeO_{3-d}$ (LSF).

An alternative approach for the application of the sol-gel route is the use of hybrid materials, instead of adding an organic substance to the solution of water soluble salts. Haas and Rose [19] classify the hybrid materials as an entire separated group. They emphasize that these materials are composed by both organic and inorganic moieties, with covalent bonds between them. Using metallic nitrate and butoxide precursors, sol-gel derived NiO-YSZ particles have been developed by Keech and co. [20]. The authors reported that after heat-treatment at 1000°C, the average particle sizes of NiO and YSZ were found to be less than 50 and 30 nm, respectively. Sol-gel synthesis of polymer-YSZ hybrid materials for SOFC is also reported in the literature [21]. Different procedures for sol-gel processing for obtaining of SOFC materials, described in an extended scientific research work [22], are presented in Fig. 1.

Despite the fact that the versatility of the sol-gel approach enables synthesis of a remarkable variety of materials, the application of this method is related to technologic limitations, stemming from the necessity of multistage production, and the demand for different precursors. Additionally, during the drying stage, the sol-gel derived films/bulk solids are very susceptible to crack-formation, unless organic additives are used [23, 24]. In the latter case, the organic supplements burn out during the subsequent sintering of the respective film, causing increased porosity. Thus, the spray techniques enable avoiding a number of the technologic operations, providing even for an one stage production.

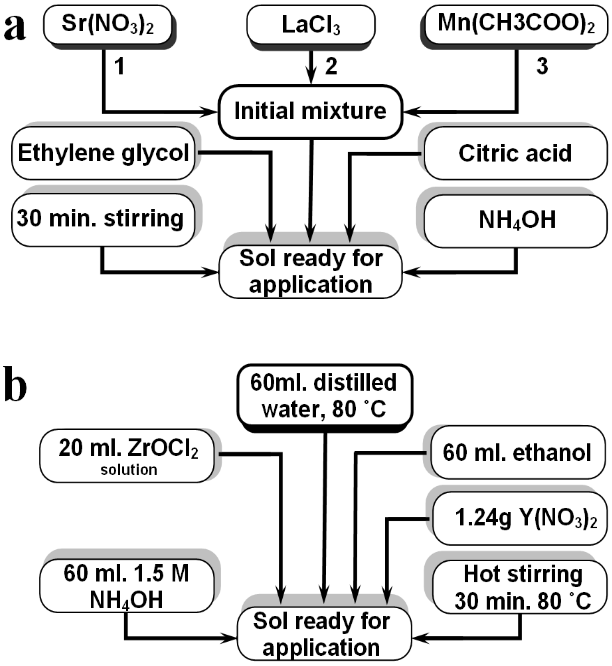

Fig. 1. Schematic presentations of sols for obtaining of SOFC material [22].

## APPLICATION OF SPRAY TECNIQUES FOR SYNTHESIS OF SOFC MATRIALS

***Spray pyrolysis.*** This method can be applied either as a Spray Pyrolysis Synthesis (SPS) for synthesis of powder materials, or in the form of a Spray Pyrolysis Deposition (SPD) for thin films [12]. The latter method enables production of layers via one stage synthesis. SPD permits combination of synthesis and SOFC assembling by direct deposition of the respective layer (cathode, electrolyte or anode) on the previous one, as is depicted in Fig. 2.

Powders composed by spherical dense particles of $ZrO_2$, stabilized by $Y_2O_3$ with a controlled size were obtained by Song et al. [25]. Their idea is to combine ultrasound dispersion with the addition of a carrier gas, during the spraying through the nozzle. According to the

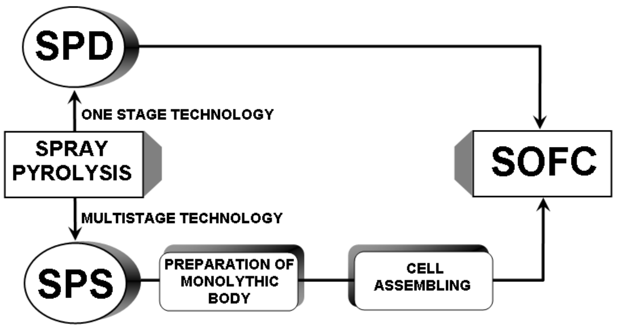

Fig. 2. Approaches for application of Spray pyrolysis for production of SOFC.

authors, this combination can unite the advantages of both techniques: higher productivity – when a carrier gas is employed, and a more narrow range of size distribution, when an ultrasound nebulizer is used. In addition, the authors have used horizontal tubular reactors, built by horizontally situated quartz tubes with diameters of 2.5 or 7.5 cm and 1.7 m of length, assembled with three separated heaters. They formed three temperature zones: with 200°C, 650-750°C, and 250 °C, respectively. A powder collector was mounted after each thermal zone. In this way only the finest particle fractions reached the exit of the reactor. As a major achievement, the authors emphasize the obtaining of uniform dense spherical nanoparticles of a 73 nm diameter by spray pyrolysis through uniform precursor drops (5 G"x488X" 8 µm of diameter) and low precursor concentration (0.01 mass %), respectively. This fraction is obtained by the authors by feeding in of the nebulizer with a 20 – 31 $dm^3$/min airflow and an electric signal with 2.66 MHz of frequency.

The SOFC cathodes are usually composed by metal oxides as $LaCoO_3$, $LaMnO_3$, or even non-stoichiometric compounds as: $La_{1-x}Sr_xCoO_{3-\delta}$, and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ [1, 26 – 28]. $La_xSr_{1-x}TiO_3$ has been prepared by the SP-method and the classical solid state synthesis route [29]. The authors remark that the spray pyrolysis approach enables production of pure phase products at significantly lower temperatures. The SP synthesis has been carried out via spraying of the precursor's suspension through the nozzle with air as carrier glass to a pot-furnace with temperatures of 550 °C in the bulk and 700 °C - on the bottom. The suspension was composed by $TiO_2$ nanoparticles, dispersed in an aqueous $La(NO_3)_3$ solution with addition of gelatin as a combustible organic compound. Afterwards, the synthesis of the obtained powder was retained for 2 hours at 700°C. The authors note the advantages of the SP technology, which enables the production of this advanced ceramic material at lower temperature, avoiding its partial destruction, at temperatures higher than 1290 °C.

Todorovsky et al. [30] have reported a successful synthesis of $Fe_2O_3$, $Y_2O_3$, $CeO_2$, $La_2Ti_2O_7$, $Y_3Fe_5O_{12}$ doped by Ce, $YFeO_3$, $LaMnO_3$ doped with Ca, $ZrO_2$ stabilized by $Y_2O_3$, $TiO_2$, $TiO_2$:$LaO_2$ and Ru(II) complexes, using spray pyrolysis deposition, combined with the sol-gel route. The last three compounds underwent characterization of magnetic and photocatalytic properties.

An interesting approach, regarding the application of thermal plasma spray pyrolysis, is proposed by Gitzhofer and co. [31]. In their paper, the authors make a brief description of various approaches for plasma induction, such as: dc/rf Hybrid Plasma Spraying (HyPS), induction plasma spraying, (IPS), Triple torch Plasma Spraying (TTPS), High-Velocity, Low-pressure dc Plasma Spraying (HVLPPS). The HyPS method combines high voltage direct current, and radio-frequency induction. Technically, the combination is performed via ionization of an argon containing gas-flux, with the same direction as the spray. Simultaneously, both flows pass through a tube, which is a carcass of a coil connected with a radio-frequency AC-generator. Alternatively, considerably high temperatures could be reached via microwave induction of the spray, during the performance of the spray pyrolysis. The advantage of the IPS-method, according to the authors, is the possibility to extend the duration of residence of the spray in the high temperature zone, by the length of the tube and its assembling with more than one coil-heater.

The most interesting among the methods described is TTPS. The method is based on obtaining of coalescent plasma by concordant contribution of three different high energy sources. The temperature of deposition and growth of the deposited film could be controlled by cooling of the support of the latter. For that purpose, the authors propose to perform the TTSP-deposition in a chamber with low pressure, and on a support with water cooling. By combination of high pressure from the nozzle, and low pressure inside the chamber, and connection of the nozzle, and the support with a direct current electric chain, the authors have succeeded to elaborate multilayer system by $La_{0.8}Sr_{0.2}MnO_3$, cathode and $Y_2O_3$/$ZrO_2$ solid electrolyte for

SOFC. The authors remark that with the combination of high pressure from the nozzle, and low pressure (vacuum) in the chamber, a significant density of the deposited films could be achieved, because of the considerable acceleration of the spray-particles. The synthesis of $Ce_{0.8}Gd_{0.2}O_{1.9-x}$ and $Zr_{0.92}Y_{0.08}O_{2-x}$ as solid electrolytes for SOFC by plasma assisted spray pyrolysis in vacuum is also proposed [32].

***Spray freezing.*** This is another spray method, which enables production of ceramic materials with desirable structures and porosity. Actually, the method has been developed as a variation of the spray tape casting. It has been used for obtaining of thin film YSZ coatings on functionally graded freeze cast NiO/YSZ SOFC anode supports [33]. Because this method is relatively new, there is not enough data for its application. Only few articles were found in the literature [34-36]. The benefits of the method are that, the speed and temperature of freezing enables to obtain amorphous or crystalline intermediated materials with desirable crystallinity. Afterwards, their structures allow for control of the porosity and the structure of the final ceramic material, without of use of additional organic substances (as in the sol-gel approach). The application of this method for obtaining of solid electrolyte materials, for intermediated SOFC is accompanied by supplemental procedures. The demand for these additional treatments originates from the necessity of spraying the solution in liquid nitrogen, in order to avoid undesirable agglomeration. After the processes of liophylisation and posterior calcination, the sintering of the material passes with pore-formation. The solid electrolytes should always be dense, and the porosity is generally undesirable in this aspect. That is the reason for accurate control of the particle size, in the cases of kryochemical synthesis. In that means, the application of the spray freezing methods should pass by intermediated operations like: milling of the obtained powder products by ball-mills, or agitation by ultrasound (sonification) of the corresponding powders, and subsequent fractional separation by sieves.

## RESEARCH AND ANALYSIS OF SOFC MATERIALS

When a new material is prepared for SOFC application, it should not only correspond to the requirements, described in Table 1, but should also excel the already existing substances. All of the materials, described in the present review, have been evaluated by the same test procedures, regardless of the method applied for their preparation. Generally, the methods can be divided in three basic groups:

- *Methods for structural and compositional characterization*: Scanning Electronic Microscopy (SEM), X-ray Diffractometry (XRD), Energy Dispersion Spectroscopy (EDS), ect. After systematic investigations via electrochemical and morphological investigations, Juhl, and co. [37] have achieved optimization of the $La_{1-x}Sr_xO3$ – YSZ composite SOFC cathode material. The combination of these analytical techniques applied has enabled the authors to decrease the polarization resistance of their SOFC-cathodes by application of a coarse layer of YSZ particles on the electrolyte surface before the composite cathode. A similar approach with a combination of SEM, EDX, and impedance spectroscopy was used by other authors **[36]** in order to determine the optimal addition of supplements, as $La_{0.5}Sr_{0.5}CoO_3$, $LaCoO_3$, or $LaNi_{0.6}Fe_{0.4}O_3$, to the main ingredient material $La_{0.8}Sr_{0.2}MnO$. Research papers, based only on morphological (via SEM), and structural (via XRD) could also be found in the literature **[1**8, 21]. Combination of these methods, with porosimetry (by BET analysis) and thermal gravimetry (TGA) was applied in order to characterize YSZ – nanoparticles obtained by sol-gel processing [37].

- *Methods for assessing electrochemical behavior and adsorption abilities:* Electrochemical Impedance Spectroscopy (EIS), at controlled temperature, and in a gaseous environment, as well as different polarization techniques, such as relaxation voltammetry, and various static and dynamic polarization techniques have been used. An entire research work is dedicated on the application of EIS to SOFC materials [38]. The electrochemical properties of the SOFC electrode materials are directly related to their adsorption capabilities. Thus, porosimetry, and/or BET-analysis is always necessary for completeness of the characterization of given electrode evaluation, as described in the literature [1, 39 - 43].

- *Methods for durability tests:* Besides the individual durability and chemical/mechanical resistivity, each material for a SOFC layer should be compatible to the rest of the elements in a given fuel cell, as a final product. That is the reason to conduct test on entire cells, instead on individual SOFC components. The most frequent problems related to the use of SOFC originate from the high temperatures necessary for their exploitation. They cause: (i)- structural changes in the cell components, due to phase transitions, (ii) - layer cracking, as consequence of the dilatation differences between the layers,(iii) - delaminating between the layers, as result of lack of adhesion, and (iv) - chemical transitions due to interactions with components with the gas streams. Even sulfur content, in the combustibles, or components of decomposition of the interconnects, could also poison the SOFC electrodes, as is described elsewhere [44, 45].

## CONCLUSIONS

The following conclusions can be drawn as a result of the presented literature review:

The sol-gel approach enables production of a large variety of SOFC ceramic materials. It can be applied by introduction of a polymerisable organic precursor or by the use of hybrid compounds. The structures of the materials can be derived from the conditions of the synthesis.

The spray pyrolysis method can be applied for elaboration of single stage technologies, without a demand for expensive equipment. In addition, it provides easy large industrial scale production.

Although the undoubted versatility of the sol-gel method, it requires organic additives to avoid crack formation, and its application is related with enhancement of film porosity, whereas the Spray Pyrolysis Deposition (SPD) enables production of dense SOFC solid electrolytes. Furthermore, the Spray Pyrolysis Synthesis (SPS) enables large scale production, with easy control of particle sizes. As a result, the Spray Pyrolysis (SP) techniques seem to be the most appropriate for large scale SOFC production, among the methods described in the present paper.

Nevertheless, the SP application can result in partial decomposition of the precursors, and in such cases, the sol-gel technique is more preferable due to the moderate temperature processing.

The complete analysis and characterization of the obtained SOFC ceramics includes electrochemical, compositional and structural characterization. Furthermore, its compatibility to the rest components of the respective SOFC should also be assessed.

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