NANOSTRUCTURED MATERIALS FOR HIGH EFFICIENCY ENERGY CONVERSION [1]

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Abstract

The aim of this work is to evidence the relations between materials properties and PEMFC (proton exchange membrane fuel cell) and SOFC (solid oxide fuel cell) performances. This work is concerned about advanced functional solid state composite materials and devices used as active component of PEMFC and SOFC systems. The main materials are structurally characterized and this materials characterization is related to PEMFC and SOFC electrical-energy macroscopic behaviours and environmental-energy-economic performances. The studied aspects show that the global performances of the PEMFC and SOFC are dependent on specific and similar material properties such as electrolyte density and its ion transport ability, catalyst dispersion homogeneity and active size clusters, anodic and cathodic nano and microstructural parameters.
Key words: Nanotechnology; Fuel cells; Nanostructured materials; Energy.

MATERIAIS NANOESTRUTURADOS PARA CONVERSÃO DE ENERGIA COM ELEVADA EFICIÊNCIA

Resumo

O objetivo deste trabalho é investigar as relações entre propriedades de materiais e o desempenho de células a combustível dos tipos de membrana polimérica e de óxido sólido, focando em materiais conjugados funcionais avançados usados como componentes ativos destas células a combustível. Estes materiais são estruturalmente caracterizados e suas características são relacionadas aos respectivos comportamentos elétrico e energético, bem como aos desempenhos energético, econômico e ambiental. Mostra-se que o desempenho das células a combustível estudadas dependem de propriedades materiais específicas e similares tais como a densidade do eletrólito, sua condutividade iônica, a homogeneidade da dispersão de catalisadores e parâmetros nano e microestruturais característicos dos anodos e catodos dessas células a combustível.
Palavras-chave: Nanotecnologia; células a combustível; nanomateriais; energia.

1 INTRODUCTION

The extraordinary mankind's development in the past two centuries (since the Industrial Revolution of the 18th Century) was based mainly on intensive use of fossil fuels (coal, oil and natural gas) in the power generation and in the transport sector. However, this continuous exploration has resulted in the reduction of the reserves these fuels, the remaining fuels have become more expensive and, above all, the harmful effects on the environment that have resulted in the global warming. Additionally, the world's demand for energy is projected to double by 2050 in function of the population growth and of the industrialization of developing countries.[1] In this scenario, extensive research and development have been made in alternative energy sources and energy efficiency conversion improvement to the sustainable growth of the world economy with the concomitant reduction of the environmental impact, mainly limiting the greenhouse gases emissions. In this context, the fuel cells could provide both electricity and thermal energy to stationary, transport and portable applications as their costs become competitive or environmental restrictions are increasing.[2]

Fuel cells are electrochemical devices that via electrochemical reactions are able to combine a fuel and an oxidant, converting the stored chemical energy of the fuel directly into direct-current electrical energy and heat. The fuel is not burned, such as in a flame, as in conventional power systems; rather, it is electrochemically oxidized. Thus, the maximum efficiency of a fuel cell is not limited by the Carnot cycle, which limits many conventional power systems such as the internal combustion engines, steam and gas turbines, and heat pumps.[3] Thus, fuel cells have been regarded as the main power generation equipment capable of increasing the energy conversion efficiency in various fields of applications.[1,2]

There are diverse fuel cell types, usually classified according to the nature of the electrolyte, which is the key component of a fuel cell, since it separates electrons and protons and provides the ionic conduction so that a useful electric current can be drawn. The main types of fuel cell are: Alkaline Fuel Cell (AFC), Direct Methanol Fuel Cell (DMFC), Molten Carbonate Fuel Cell (MCFC), Phosphoric Acid Fuel Cell (PAFC), Proton Exchange Membrane Fuel Cell (PEMFC) and Solid Oxide Fuel Cell (SOFC). Among these, the PEMFC and the SOFC are clearly the two fuel cell types that have been more emphasized for the most diverse applications and they are in pre-commercial stage, with great perspectives for cost-reducing.[3-5] Figure 1 shows examples of the PEMFC and SOFC units as well as of schemes and stacks. On both fuel cell types, the heart of the fuel cell is a solid-state composite material-device of which emerge the respective fuel cell behaviors. This composite component is the Electrolyte-Electrodes Assembly (EEA), better known as MEA (Membrane Electrode Assembly) mainly for PEMFC, which is composed by a solid electrolyte sandwiched by two electrocatalysts-electrodes, becoming the main component that holding the most significant influence on overall cost, useful life and fuel cell performance.[6-9]

Besides of the MEA and its components, there are others materials, components and devices (e.g. bipolar plates and interconnects, gas diffusion layers), that are important to fuel cell performances and in all the cases the need to minimize material-component resistivities, in order to reduce the ohmic losses in the fuel cell stack, has a major impact on the selection, development and processing of the materials and fuel cell components.[10]

An essential aspect of the fuel cell technologies is the fact that its main components are either tend to be nanostructured, since the electrochemical phenomena that give

rise to the macroscopic behavior of the equipment are fundamentally characteristic phenomena of interfaces and thus the use of materials at the nanoscale allows it to maximize these interfaces.[7,10,11] This work is concerned about advanced functional solid state composite nanostructured materials and devices used as active component of PEMFC and SOFC systems, as part of research developed in Cepel (Electric Power Research Center).
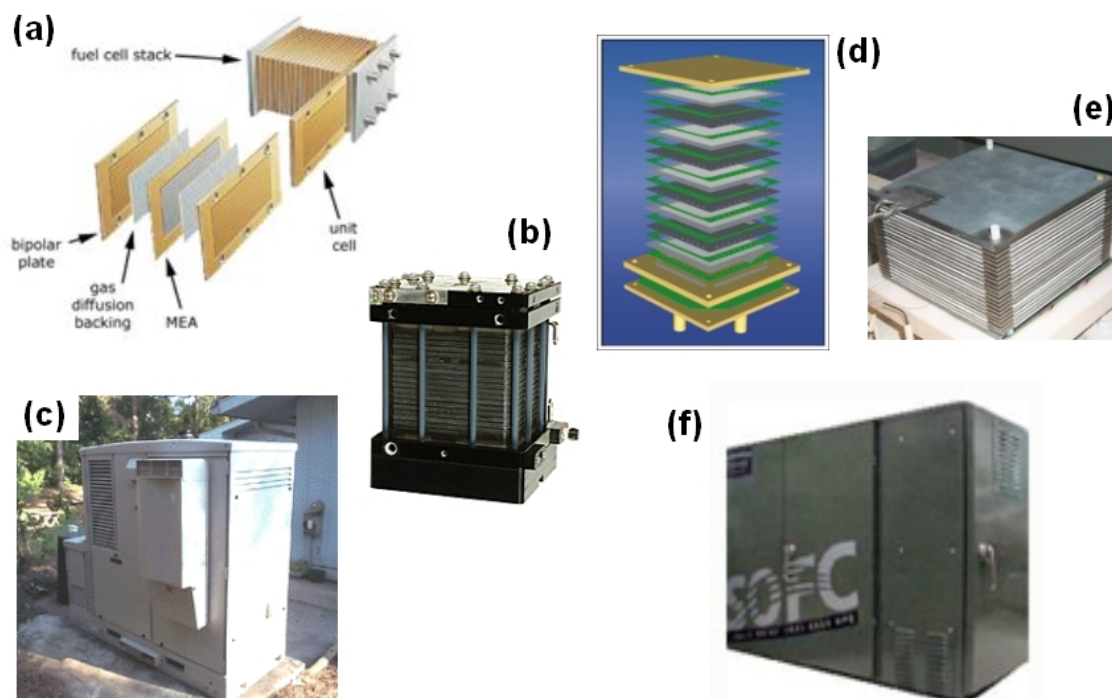

Figure 1. PEMFC (a, b, c) and SOFC (d, e, f) systems: (a) and (d) stack schemes; (b) and (e) stack examples; (c) and (f) generation units.[2,4,5]

2 DEVELOPMENT

The latest technological trends for PEMFC and SOFC are, respectively, that able to operate at higher temperature (HTPEMFC, in the range 90-130^{0}C), and that able to operate at temperature lower than the usual (ITSOFC, Intermediate Temperature SOFC, in the approximate range 650-800^{0}C). In the first case, the improvements to the membrane component of PEMFCs are a crucial requirement for advances in this technology. In fact, the usual membrane (Nafion, DuPont, shown in Figure 2) is limited to operating temperatures below 100^{0}C due to the tendency of the membrane to dehydrate. Thus, there is an intense development of high-temperature electrolytes to PEMFCs and this ability can result in higher fuel cell system efficiency and lower cost, and less sensitive to the hydrogen purity. Higher temperature operation allows the use of smaller radiators in automobiles and more useful waste heat for stationary applications. Other aspect is the improvement of the homogeneity degree of the electrocatalyst dispersion on the electrolyte-membrane.[11-13] In fact, as shown in Figure 2(a-c), there is a need for this improvement in the construction of MEAs. Single PEMFC, as shown in Figure 2(d), are used in the research and characterization of PEMFC materials and components. Figure 3 shows details of the surfaces of the MEA and the GDL (gas diffusion layer). We can see in Figure 3(b) electrocatalyst particles of various sizes, which should have minimized their sizes

(hence the tendency to nanostructuring) to maximize the area or triple phase boundary (formed between the electrocatalysts, the electrolyte and the gaseous phases). Also the GDL (Figure 3(c)) shall be produced from pure and finely divided carbon to provide high electrical conductivity and in this sense, the use of carbon nanotubes have been considered.
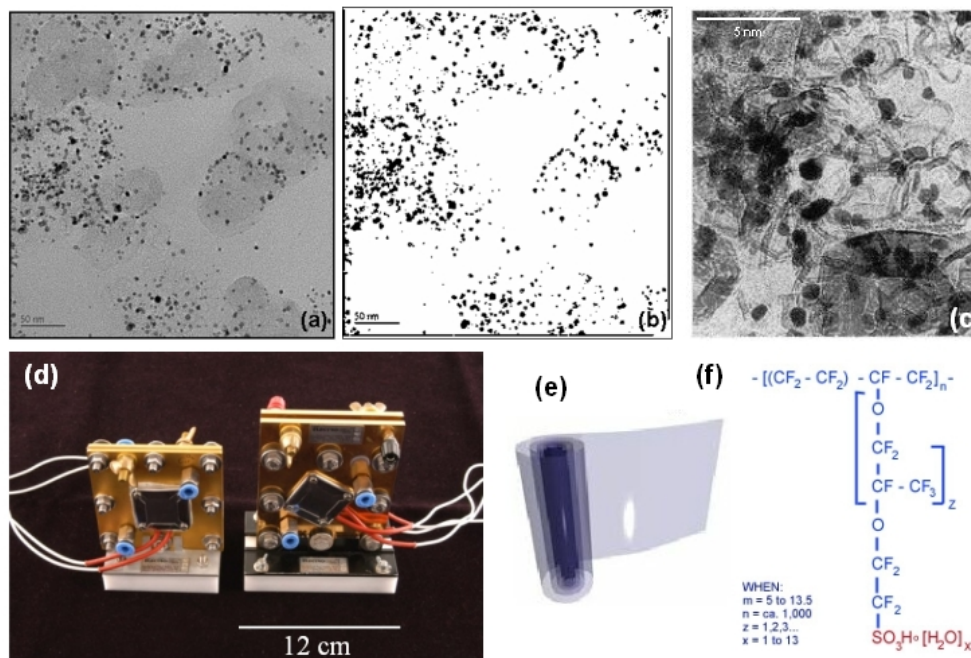

Figure 2. PEMFC features: (a), (b) and (c) transmission electron microscopy images show heterogeneous distributions of electrocatalysts and clusters formations; (d) single fuel cells to performance and material-components tests; (e), (f) Nafion® and its chemical structure.
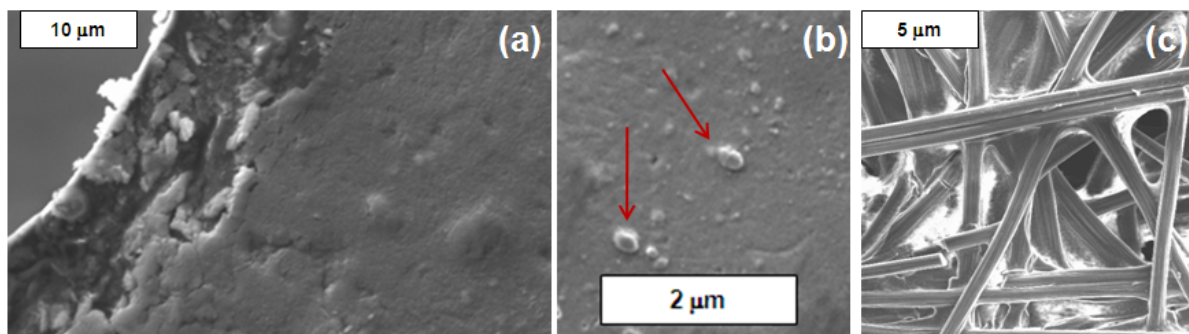

Figure 3. PEMFC features: (a) MEA structure; (b) MEA details shown the electrocatalyst particles; (c) GDL microstructure shown the carbon fibers.

Another PEMFC material component that has demanded research and development is the bipolar plate, which is a multifunctional component in PEMFC stacks, collecting and conducting the electrical current from single fuel cell to single fuel cell, and distributing the reacting gases (H_2 and O_2) to the respective fuel cell electrodes.[14] The basic requirements for the bipolar plate material include high electrical conductivity, good mechanical strength, and good corrosion resistance. Bipolar plates are responsible for most of the mass and volume of a fuel cell stack.[14] Thus, the reduction in the thickness of these components will enable a reduction in size of the stack, this being of interest from both technical and commercial points of view. The most commonly used bipolar plate material is graphite, which presents ideal corrosion resistance and electrical conductivity.[15] Nevertheless, its high cost and the

need of intensive machining to form the flow channels limit this material for applications involving high-volume manufacturing. Additionally, graphite is very brittle and lacks mechanical strength, and therefore the thickness of the plates cannot be reduced. This results in thicker plates with bulkier sizes and more elevated weights.[15] In light of these problems, there is great interest in the replacement of the graphite as base material of the PEMFC bipolar plates. Several alternatives to replace the graphite have been considered, such as conductive polymers, carbon–polymer composite materials, graphite-filled polymer, carbon–carbon composite materials, and metals and metallic alloys.[15] Considerable attention has been recently given to metallic-based bipolar plates due to their high electrical conductivity, acceptable material cost, high strength, low gas permeability, and applicability to mass production. The major disadvantage of metals is that they are very susceptible to corrosion when exposed to the acidic and humid environments usually containing sulphate, chloride and fluoride ions, and reactant gases inside the PEMFC.[16] The corrosion can cause the formation of a passive surface layer, which increases the electrical interfacial contact resistance (ICR), while the metal dissolution can contaminate the membrane and electrocatalysts. The passivation/dissolution of metallic bipolar plates would cause considerable power loss.[16] In order to avoid or minimize the problems associated with the corrosion of metallic materials, one solution is to coat the metallic bipolar plates with protective and nanostructured conductive coatings. Figure 4 shows graphite-based and metallic bipolar plate examples.
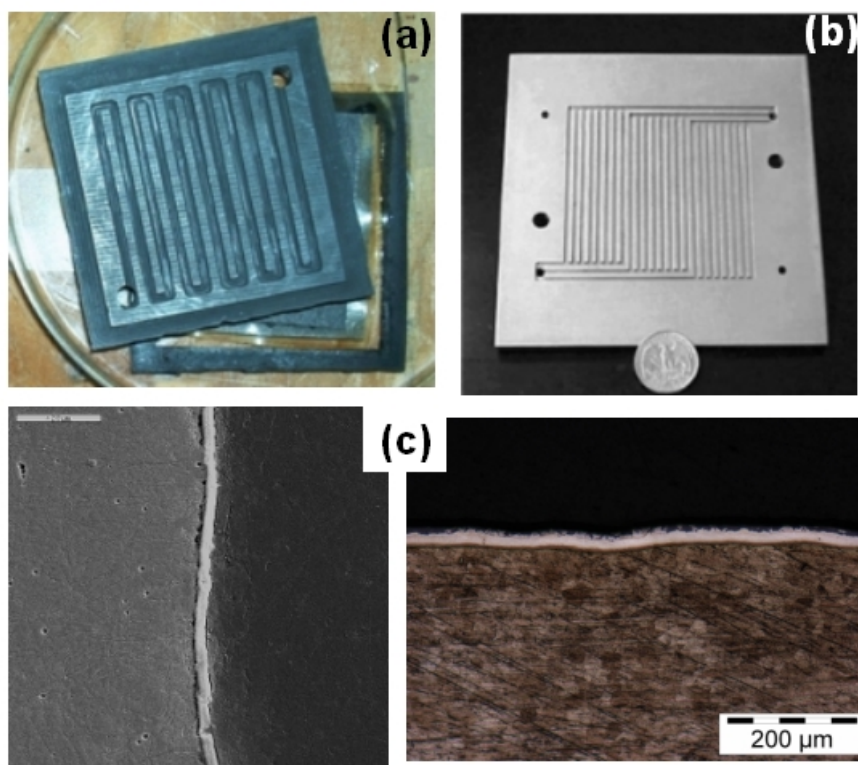

Figure 4. PEMFC bipolar plates: (a) graphite-based bipolar plate; (b) metallic bipolar plate, (c) scanning electron and optical microscopy images show different coatings on stainless steel bipolar plates.[17]

Figure 5(a) shows the average values of ICR of the as-received samples.[17] The ICR decreases markedly with increasing compression between the plates. In practical conditions this compression is limited to a value around 140 N/cm^2 to prevent

damage to other fuel cell components. Figure 5(b) shows the performance curves of the single PEMFC made with AISI316L TiN-coated bipolar plates after 500 hours of operation, as compared to the performance of this fuel cell in the initial conditions. A possible ageing effect of the fuel cell with time was shown by a small decrease (5% or less) of the voltage values for the same current densities, especially in the ohmic polarization region (50 to 300 mA/cm^2). [17]
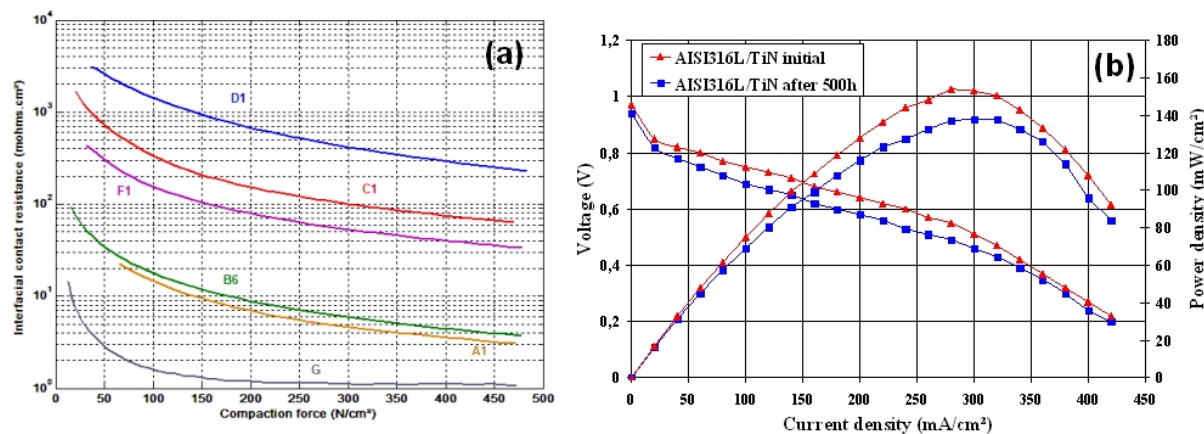

Figure 5. (a) ICR values against compression force. Samples: A1 (titanium nitride), B6 (chromium nitride), C1 (ion nitrided), D1 (diamond-like carbon), F1 (without coating) and G (conventional graphite for PEMFC bipolar plates); (b) PEMFC with AISI316L/TiN plates - Initial and after 500 hours of operation.[17]

In the case of SOFC technology, Figure 6(a) shows photomicrographs of a SOFC electrolyte-electrodes structure emphasizing the dense character of the electrolyte and the porosity nature of the electrodes. The research and production of EEA have benefited from the developments of the nanoscience and nanotechnology areas.[18] In fact, several research lines have been dedicated to the development of anode materials which can directly electro-oxidize hydrocarbon fuels at intermediate temperatures (for ITSOFC) without carbon deposition, and to the development of cathode materials, which are active for oxygen electroreduction at these reduced temperatures. Figure 6(b) shows SOFC assembly schemes and Figure 6(c-d) shows some components of a SOFC stack.

Each solid oxide single fuel cell includes yttria stabilized zirconia (YSZ), containing typically 8mol% Y_2O_3, as the electrolyte; a ceramic-metal composite (cermet) comprised of Ni and YSZ as the anode; lanthanum strontium manganite (LSM) as the cathode; the interconnect material is alkali doped lanthanum chromite ($LaCrO_3$); and glasses or glass-ceramics system as sealant for planar design.[18]
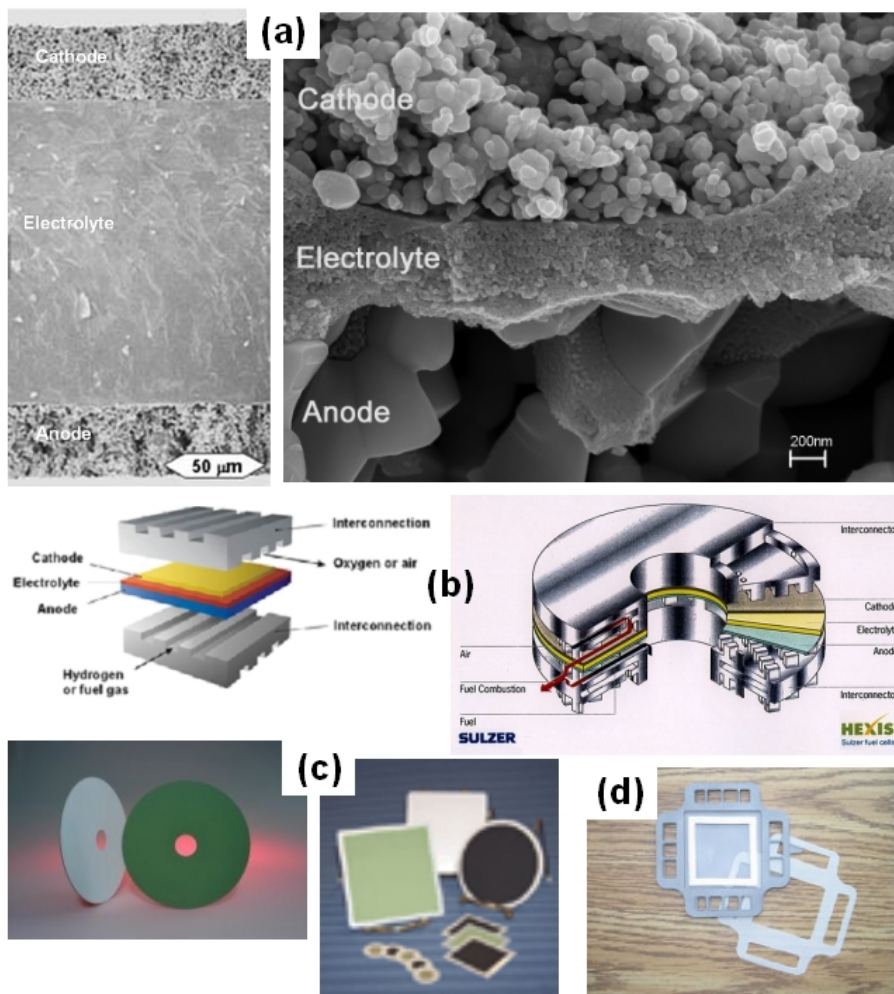
Figure 6. SOFC features: (a) scanning electron microscopy images show the EEA structures; (b) fuel cell assembly schemes; (c) EEA components, (d) ceramic interconnector.[8,10,23]

In addition to the above comments about the SOFC materials and components the Figure 7 shows examples of SOFC ceramic powders, which have been prepared by several methods such as, solid-state reaction, sol-gel, hydrothermal synthesis, spray-drying, co-precipitation, combustion and gel-combustion, sonochemical process, and Pechini method.[18-21] Figure 7(a) and Figure 7(b) shown respectively photomicrographs of YSZ (yttria stabilized zirconia) synthesized by GNP (glycine-nitrate process, a combustion technique) and by Sol-Gel method. In this case the interest is to produce equiaxial and fine particles that result in the production of full-densified YSZ ceramic, as shown in the Figure 8(a-b). On the other hand, the same synthesis methods are used to preparation of nanostructured powders for SOFC cathodes and anodes, as the shown in the Figure 7(c), which provide the production of high porosity SOFC electrodes.[22, 23]
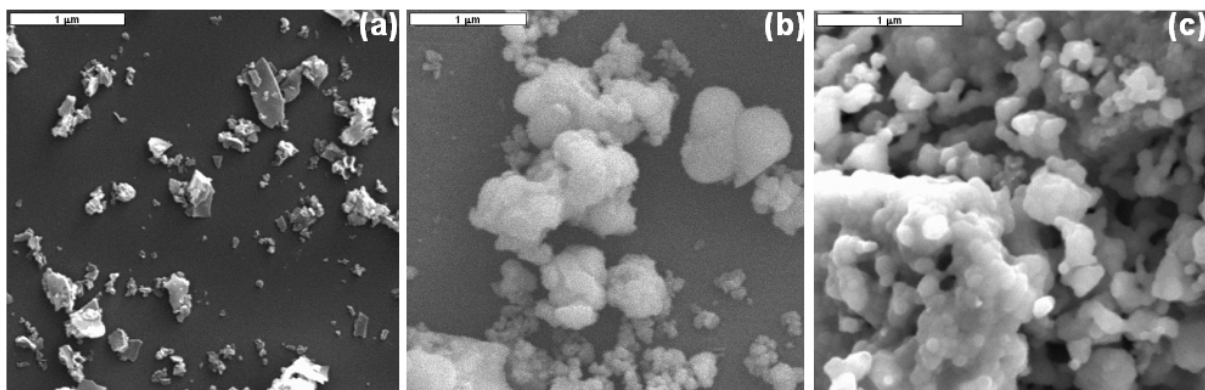
Figure 7. SOFC powders: (a) YSZ synthesized by GNP; (b) YSZ synthesized by Sol-Gel method; (c) lanthanum manganite cathode synthesized by combustion method.
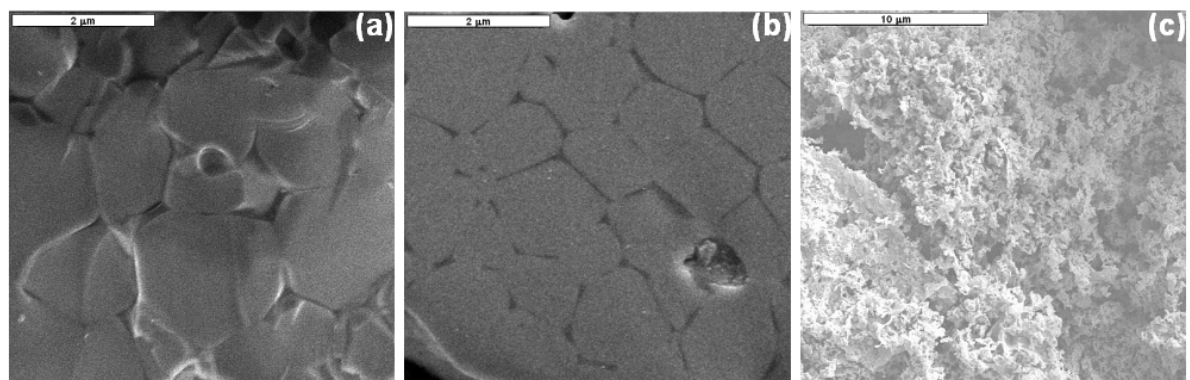

Figure 8. SOFC material microstructures: (a) and (b) full-densified YSZ ceramic; (c) porosity cathode ceramic.

Also the SOFC ceramic interconnector (Figure 6(d)) is produce from synthetic nanopowders and as the electrolyte it must be a full-densified component with preferably nearly 100% electronic conduction, adequate stability in terms of dimension, microstructure, chemistry, and phase at operating temperature around 800-1000^{0}C in both reducing and oxidizing atmospheres, since they are exposed to oxygen on one side and fuel on the other. Interconnect should display exceptionally low permeability for oxygen and hydrogen to minimize the crossover direct combination of oxidant and fuel during cell operation. Thermal expansion coefficient (TEC) of interconnect should be comparable to those of electrodes and electrolyte between ambient and operating temperatures, so that the thermal stress developed during stack startup and shutdown could be minimized. Figure 9 show photomicrographies (SEM) characteristics of the microstructures of lanthanum chromite-based ceramic studied systems. The distributions of porosity are seen clearly, either in incipient sintering conditions or in the best densification microstructure, Figure 9(d), in which can be seen the intergranular porosity incidence. These observations are reflected on the electrical and dimensional characteristics shown in Table 1. The electrical conductivity values are in the range characteristic of lanthanum chromites mono- and dual-doped, and great variability. The usually considered as acceptable TEC values are in the range of 9.9 x 10^{-6} to 10.6 x 10^{-6} ^{0}C^{-1} [24]. Particularly the La$_{0.90}$Sr$_{0.10}$Cr$_{0.95}$Mg$_{0.05}$O$_3$ and La$_{0.90}$Ca$_{0.05}$Sr$_{0.05}$Cr$_{0.95}$Mg$_{0.05}$O$_3$ systems had presented the more adequate TEC values.[24] The lanthanum chromite-based ceramics doped with Sr (La$_{0.90}$Sr$_{0.10}$CrO$_3$ and La$_{0.90}$Sr$_{0.10}$Cr$_{0.95}$Mg$_{0.05}$O$_3$) had presented greater densification degree than those doped with Ca (La$_{0.90}$Ca$_{0.10}$CrO$_3$ and La$_{0.90}$Ca$_{0.10}$Cr$_{0.95}$Mg$_{0.05}$O$_3$). In fact, the

densification mechanism depends on of the metal dopant, and with the Sr the transient liquid phase formed ($SrCrO_4$), beyond it exists in bigger proportion, it results in better wetting condition, intensifying the densification process.
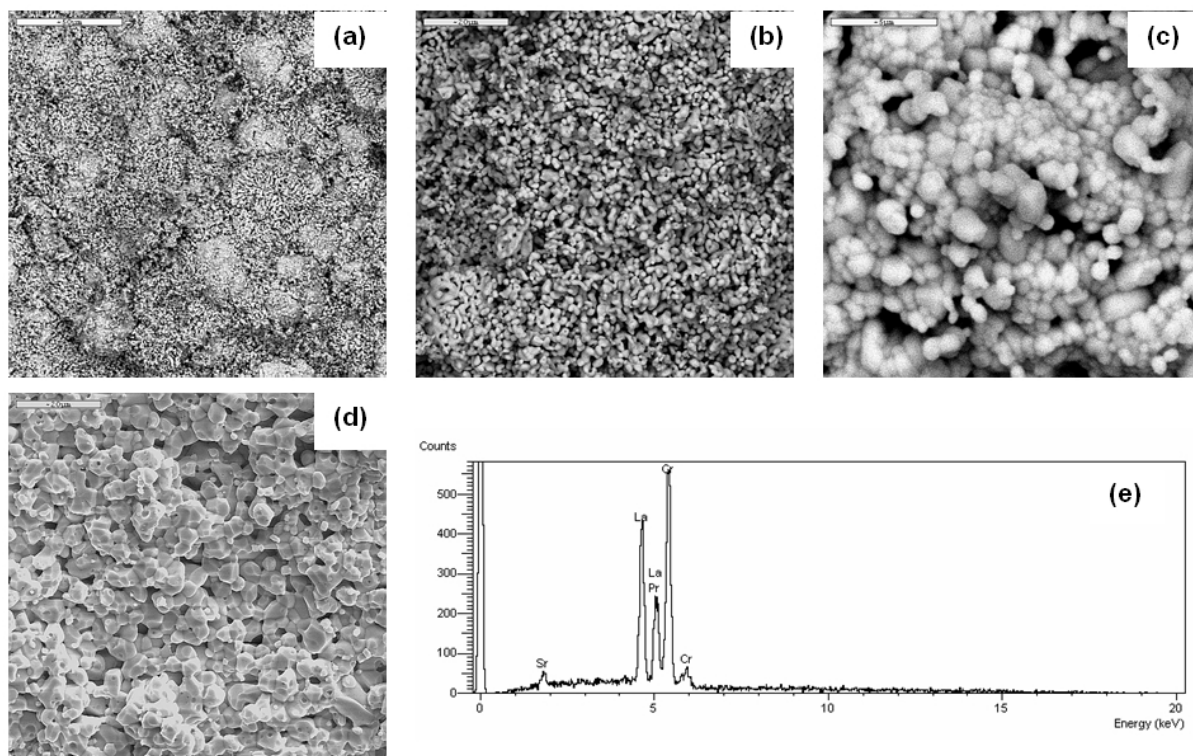

Figure 9. Microstructural characterization (SEM) of lanthanum chromite-based ceramics in different sintering conditions: (a) $La_{0.90}Ca_{0.10}CrO_3$ -1200^{0}C, (b) $La_{0.90}Sr_{0.10}CrO_3$ - 1300^{0}C, (c) $La_{0.90}Sr_{0.10}Cr_{0.95}Mg_{0.05}O_3$ - 300^{0}C, (d) $La_{0.90}$ $Ca_{0.05}Sr_{0.05}Cr_{0.95}Mg_{0.05}O_3$ - 1400^{0}C, (e) EDS analysis result of the microstructure shown in Figure 9(d).

Table 1 – Microstructural (average grain size and densification degree) and performance (electrical conductivity and thermal expansion coefficient) parameters of the lanthanum chromite-based ceramics

Chemical composition (mol%)	Average grain size (μm)	Densification degree (%)
$La_{0.90}Ca_{0.10}CrO_3$	10.20 ± 1.50	92.1 ± 0.3
$La_{0.90}Sr_{0.10}CrO_3$	11.10 ± 1.30	94.2 ± 0.3
$La_{0.90}Ca_{0.10}Cr_{0.95}Mg_{0.05}O_3$	9.30 ± 1.60	94.8 ± 0.4
$La_{0.90}Sr_{0.10}Cr_{0.95}Mg_{0.05}O_3$	9.40 ± 1.10	95.4 ± 0.3
$La_{0.90}Ca_{0.05}Sr_{0.05}Cr_{0.95}Mg_{0.05}O_3$	8.90 ± 1.70	96.1 ± 0.3
	Electrical conductivity (S/cm)	**Thermal expansion coefficient** (x 10^{-6} ^{0}C^{-1})
$La_{0.90}Ca_{0.10}CrO_3$	16.4 ± 1.9	9.1 ± 0.5
$La_{0.90}Sr_{0.10}CrO_3$	18.5 ± 1.7	8.8 ± 0.6
$La_{0.90}Ca_{0.10}Cr_{0.95}Mg_{0.05}O_3$	21.3 ± 1.9	9.7 ± 0.4
$La_{0.90}Sr_{0.10}Cr_{0.95}Mg_{0.05}O_3$	22.1 ± 1.6	9.8 ± 0.2
$La_{0.90}Ca_{0.05}Sr_{0.05}Cr_{0.95}Mg_{0.05}O_3$	21.8 ± 3.4	9.9 ± 0.5

As has been emphasized throughout this work, currently the central challenge of SOFC technology consists of depositing a dense thin film electrolyte on a porous electrode and ensures appropriate properties at the interface of this system, as well as in the respective bulks. Figure 10 illustrates this situation, where we see in Figure 10(a) the structure of the bilayer, produced at the CEPEL by tape casting, and

the region expanded in Figure 10(b) shows the different microstructural characteristics of these components and of the interface between them.
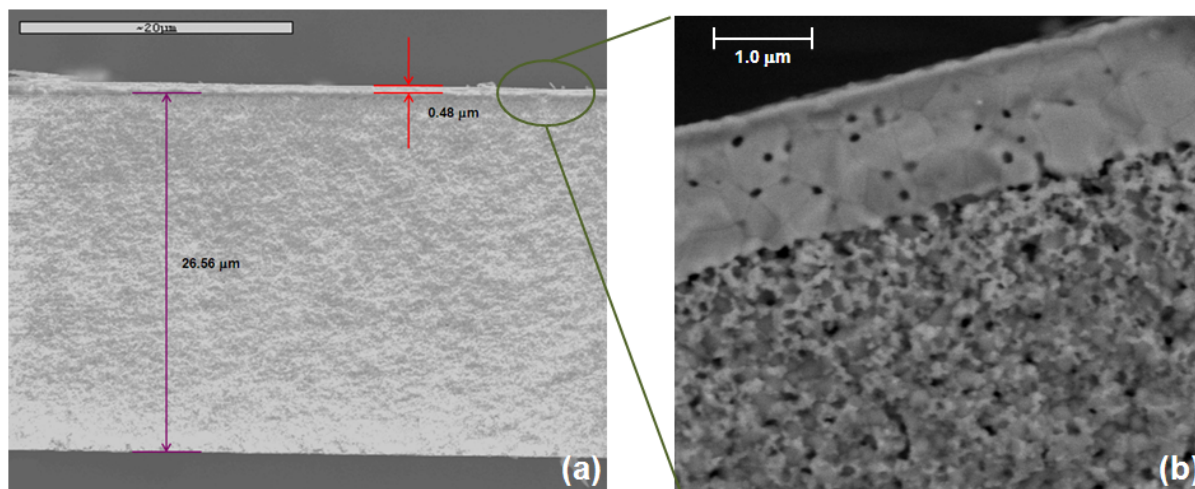

Figure 10. Bilayer component of an electrolyte-electrodes assembly of solid oxide fuel cell: (a) microstructure showing the typical dimensions involved; (b) enlarged detail of the interface region showing significant microstructural differences.

3 CONCLUSIONS

An overview of research works developed by CEPEL, opportunities and challenges of the PEMFC and SOFC technologies was presented. The performances of the PEMFC and SOFC are dependent on specific and similar material properties such as electrolyte density and its ion transport ability, catalyst dispersion homogeneity and active size clusters, anodic and cathodic nano and microstructural structures, which influence the complexity of the electrical and mass transport phenomena that determine the energy and environmental-friendly (greenhouse gas reduction) character and performances of the fuel cell systems. Thus, system design, performance and cost depend on the properties of innovative and advanced nanostructured materials. The careful design and manufacture of these materials is essential to fuel cell system integration and performance, and may ultimately determine the success or failure of these high efficiency energy conversion technologies. Particularly, it was shown examples and technological trends that show that the technologies of fuel cells are strongly dependent on the properties of surfaces and interfaces, which tend to be nanostructured in order to increase the performance of these electric power generators.

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