Abstract

World energy demand is continually growing. Nowadays, this demand is satisfied by fossil fuels as oil, natural gas and coal. These energy sources are non-renewable and its use is harmful for the environment.

The utilization of hydrogen along with renewable sources of energy is an alternative to the current energy matrix. Solid Oxide Fuel Cells (SOFCs) generate electrical energy and heat using hydrogen as fuel although they can also operate with methane and carbon monoxide. This characteristic is particularly attractive for its use in the transition period between fossil fuels and hydrogen. SOFCs can generate a wide range of electrical power and the generated heat can be used for co-generation in a gas turbine.

Conventional SOFCs consist of $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) cathode, Ni-$(ZrO_2)_{1-x}(Y_2O_3)_x$ (Ni-YSZ) anode and $(ZrO_2)_{1-x}(Y_2O_3)_x$ (YSZ) electrolyte. The high temperatures (in the range 800-1000 ºC) needed for operation (i.e. to allow oxygen ions conduction through conventional electrolytes), require high cost interconnecting materials such as lanthanum chromites ($LaCrO_3$). The employment of thin electrolytes ($\sim$ 15 μm) and new materials as gadolinium doped ceria (GDC) lower the operation temperature to the 500-700ºC range in the so-called intermediate temperature SOFC (IT-SOFC), and permit the use of low-cost metallic interconnectors. However, cathode overpotential becomes important at these temperatures, decreasing the cell performance. Therefore it is necessary to improve cathode performance optimizing its microstructure and composition. Most of research effort only focuses on cathode composition, so only few works deal with its microstructure. Accordingly, the aim of this work is to study the influence of IT-SOFC cathode nano/microstructure on its electrochemical performance.

In order to do that, different methods to prepare nanostructured $La_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_{3-\delta}$ powders were investigated. In particular, a new chemical route based on acetyl acetone and hexamethylenetetramine (HMTA method) was developed. Sub-micrometer LSCFO powders were obtained at a temperature at least 100 °C lower than the needed for others methods as Acetate and nitrate-citrate (this one commonly used in literature to obtain LSCFO powders).

Cathode Area Specific Resistance (ASR) values strongly depend on cathode nano/microstructure and morphology, which is determined by starting-powder preparation method. ASR values can vary more than two orders of magnitude for identical composition. In particular, cathodes prepared by HMTA method present ASR values that are even lower than those reported for the best known cathodes for IT-SOFC like $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO), reaching values as low as 0.05 Ωcm^2 at 600 °C and 0.18 Ωcm^2 at 550 °C. This last ASR value is close to the proposed target of 0.15 Ωcm^2 for IT-SOFC cathodes.

The oxygen reduction reaction (ORR) limiting mechanisms in nanostructured cathodes prepared by Acetate and HMTA methods were investigated by impedance spectroscopy measurements performed at different temperatures (400-600 °C) and oxygen partial pressures ($-3 < \text{Log } pO_2 < 0$). ORR limiting steps are oxygen diffusion in the cathode bulk and pure

oxygen gas diffusion at high temperatures and co-limited with dissociative adsorption at low temperatures. This study also pointed out that the high electrochemical performance observed for Acetate and HMTA cathodes is owned to the presence of nanocrystallites in cathode material. This is a novel contribution to high performance IT-SOFC cathodes design.

Partial transformation to the ordered brownmillerite phase ($La_{0.8}Sr_{1.2}Co_{1.6}Fe_{0.4}O_5$ - spacial group *Icmm*) was observed in powders prepared by Acetate and HMTA methods after a reductive thermal treatment. The transformation only occurred in part of the sample, coexisting both the original perovskite and the new formed brownmillerite phases inside the same grain. This transformation was reverted with a thermal treatment under oxidizing atmospheres (O_2 or 20 % O_2/80 % N_2). The particular microstructural characteristics of these powders are responsible of the observed behavior, being this the first time that ordered brownmillerite phase is reported for the $La_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_{3-\delta}$ composition.

ASR values evolution from a LSCFO/GDC/LSCFO cell prepared by Acetate method was investigated by *in-situ* impedance spectroscopy over a continuous measurement period of 1000 hours in air at 500 °C, in order to evaluate the practical application of nanostructured cathodes. Total cathode ASR value augments $\sim 25\,\%$ in the first 700 hours of measurement but it stabilizes in the next 300 hours. Even though the ASR degradation rate observed in the first 700 hours of operation is much larger than the recommended one, the final stabilized value exhibited in the last 300 hours of operation is similar to those reported for the best known cathodes for IT-SOFC like BSCFO. No evidence of significant change in crystallite size was found after 1000 hours measurement period, despite the exhaustive microstructural characterization performed. Moreover, nanocrystallites (to which high cathode performance was attributed) were still observed after that period. This indicates that cathode ASR value degradation is not related to changes in its nanostructure. These promising results promote the practical application of nanostructured cathodes in a commercial IT-SOFC.