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Synthesis of Ceramic Nanometric electrocatalysts

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The technological processes and devices, that are necessary to operationalize the new energetic alternatives in order to guarantee the non-polluting perennial supply of energy in view of the increase demands of our society, are strongly dependent on the development of new materials [1]. In special, the use of hydrogen energy requires the adequate performance of fuel cells, which makes the efficient conversion of a fuel's chemical energy into electric energy and heat. Among the various types already invented, solid oxide fuel cells – SOFC – are particularly attractive, because of their elevated operation temperature, with ample liberation of superheated water vapor due to exothermic electrochemical reactions, presenting great industrial interests. An unusual additional advantage is related to the innovation concerning the fact that the generation of electric energy becomes a high-aggregated value subproduct within a process in which the main objective is the electrochemical conversion of methane into C2-type hydrocarbons, such as ethylene and ethane [2]. Whether for its conventional use of electric energy and heat generation [3] or even to work in a reversible way for the production of hydrogen by electrolysis [4]; whether for use as a reactor for the electrochemical conversion of methane [2] or even to guarantee the direct utilization of carbonaceous fuels [5,6], the fabrication process of innovative solid oxide fuel cells begins with the synthesis of electrocatalysts used to make their electrodes, specially the anode.

The SOFC anodes that are made with simultaneous and differentiated working objectives are appropriately denominated multifunctional anodes. The challenges, in this case, are multiple and include, at least:

1. Regarding the Microstructure:
    a. To comprise materials with chemical composition and phases that are adequate for the required electrocatalytic behavior and able to be kept stable during the entire utilization of the temperature range;
    b. To be processed with the use of materials possessing ceramic powders with nanometric particle size, since this will influence the sintering kinetics;
    c. Its structural constitution be such that the crystallite size is also of a nanometric order of magnitude to ensure that a refined crystalline structure will be obtained;
    d. To be porous to allow the percolation of the reaction gases with porosity of the order of or superior to about 40%;
    e. That the porosity is of the interconnected type, presenting tortuosity, capable of creating a pathway for the reactive fuel gas throughout the anode bulk and even to the interface with the electrolyte;

2. Regarding the Stability and Compatibility:
    a. To present chemical stability, not liberating chemical elements that react thus creating intermediate phases capable of competing with the electrocatalytic behavior required or to interfere with the diffusivity of O^{2-} ions;
    b. To present morphologic stability during use, in order to avoid any significant modification on the type, size and distribution of the microstructural species initially existent;
    c. To present thermo-mechanical stability during use, resultant from an anode that possesses thermal expansion coefficient with value close to the other components of the electrolyte-electrodes assembly;
    d. To be resistant to the presence of contaminants eventually present in the fuel, particularly sulfur;

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e. If carbonaceous fuels are to be used, resistance to carbon coking and clogging is required, otherwise the anode might become clogged, deactivated and broken apart;

3. Regarding the Conductivity:
    a. The anode must preferably present mixed conductivity, simultaneously ionic and electronic, to increase the triple phase boundaries where the desired electrochemical reactions take place, in addition to the anode-electrolyte interface;

4. Regarding the Electrocatalytic Activity:
    a. To present suitable kinetics at the operational temperature to promote the fuel oxidation and liberation of the water vapor produced;
    b. To eventually be multifunctional in order to simultaneously promote the fuel oxidation with the resultant production of electrons and the fuel's electrochemical conversion into chemical compounds of interest;
    c. To keep the triple phase boundaries sound and active during utilization, for being the main sites where the electrochemical reactions of interest take place;

For the conditions above to be reached, the synthesis of the ceramic powder to be utilized as an electrocatalytic element in the anode has to be made in an extremely controlled way, with respect to the specific surface and particle size. Table 1 presents such results for cerium aluminate, used as SOFC anode with the direct utilization of ethanol [7], aiming to efficiently produce electricity without carbon coking. Figure 1 presents total conductivity values for multifunctional anode composed of lanthanum aluminate that is able to promote the direct oxidation of methane and its electrochemical conversion into C2-type hydrocarbons [8].

Table 1: Surface area, particle size and crystallite size of the ceramic electrocatalytic powder for SOFC anode to operate with the direct utilization of ethanol [7]. The sample nomenclature refers to cerium aluminate calcined in air at: CeAl3: 300ºC; CeAl4: 400ºC; CeAl6: 600ºC; CeAl8: 800ºC; CeAl9: 900ºC and CeAl9RH: reduced under hydrogen at 900ºC.

Sample	Specific Area (m^2 g^{-1})	Particle Size (nm)	Crystallite Size (predominant phase) (nm)
CeAl3	34.9 ± 0.0243	29.0	31.75($CeAlO_3$)
CeAl4	28.9 ± 0.2119	30.7	30.22($CeAlO_3$)
CeAl6	22.1 ± 0.1251	38.5	17.33($CeAlO_3$)
CeAl8	17,3 ± 0.0313	48.1	7.65(CeO_2)
CeAl9	16.8 ± 0.0026	49.5	13.70(CeO_2)
CeAl9RH	7.4 ± 0.0026	134.9	64.20($CeAlO_3$)

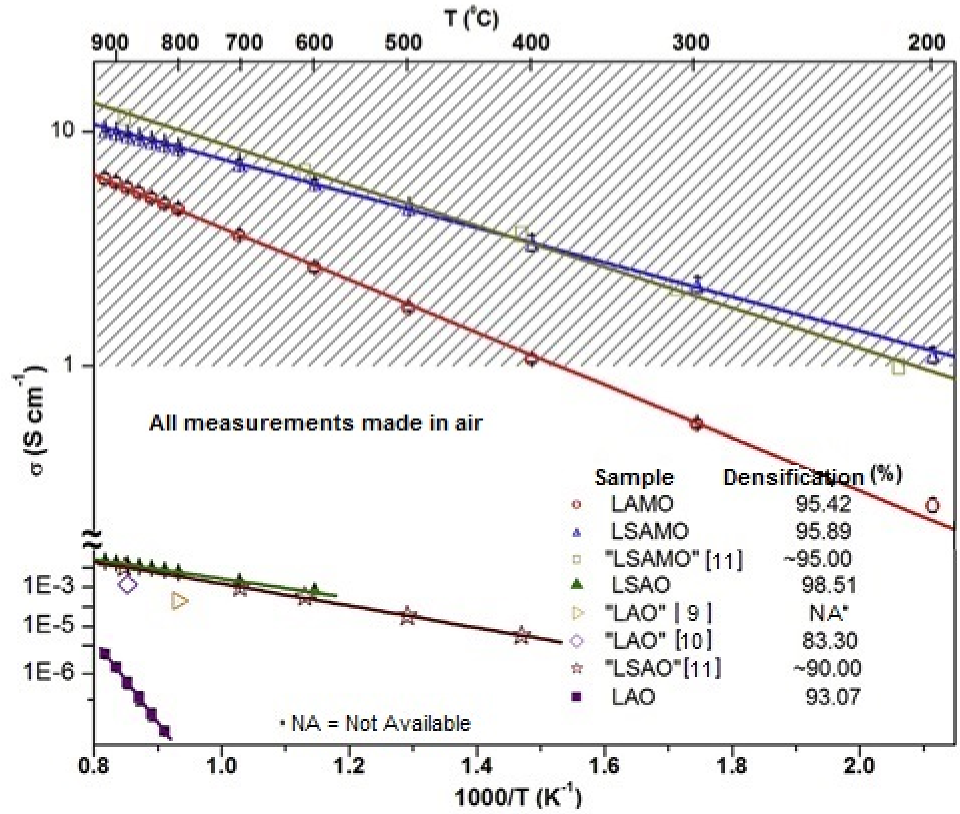

Figure 1: Total conductivity as a function of temperature for densified ceramic powder samples for SOFC multifunctional anodes [8]. The sample nomenclature refers to lanthanum aluminate: LAMO: doped with manganese; LSAMO: doped with manganese and strontium; LSAO: doped with strontium; LAO: intrinsic. The shaded area highlights the level from which conductivity reaches practical interest.

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