SYNTHESIS OF $Pr_{0.70}Sr_{0.30}MnO_{3\pm\delta}$ AND $Nd_{0.70}Sr_{0.30}MnO_{3\pm\delta}$ POWDERS BY SOLUTION-COMBUSTION TECHNIQUE

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Powders of $Pr_{0.70}Sr_{0.30}MnO_{3\pm\delta}$ *(PSM) and* $Nd_{0.70}Sr_{0.30}MnO_{3\pm\delta}$ *(NSM) compositions, which are being investigated as alternative cathode materials for intermediate temperature solid oxide fuel cells. The compositions were synthesized by a solution-combustion method using metal nitrates and urea as fuel. The combustion synthesis is a really suitable synthesis route to achieve, at low temperatures and fine and homogeneous powders. Single phase pseudo-perovskites were obtained by X-ray diffraction after heat treatment of PSM and NSM powders at 900 ºC. The synthesized and milling powders had an average particle size between 0.27 to 0.07 μm. Chemical analysis of the powders calcined was done by X-ray fluorescence and morphological analysis by scanning electron microscopy. The results had been compared with literature, indicating characteristics adjusted for preparation of ceramic suspensions.*

Keywords: combustion synthesis, powders, cathode, solid oxide fuel cell.

INTRODUCTION

Solid Oxide Fuel Cells (SOFC) are identified as clean, efficient and high capacity promissory alternative energy devices as they have demonstrated high-energy conversion efficiency, high power density, extremely low pollution, in addition to flexibility in using hydrocarbon fuel (1-3).

A major obstacle for commercial applications of SOFC still is high cost, both in terms of materials and processing (1-2). Therefore, it is also studied Intermediate Temperature Solid Oxide Fuel Cell (ITSOFC), which new materials, can significantly reduce the cost of SOFC (4-6).

This instigates research in the area of novel synthesis ceramic powders to cathode, anode, interconnector and electrolyte materials used in this technology. A number of approaches such as, solid-state reaction, sol-gel, hydrothermal, spray-drying, freeze-drying, co-precipitation, polymer precursor method and solution-combustion have been used for ceramic powders preparation and processing (7,8).

The solution-combustion has been utilized for the synthesis of various oxide powders such as ferrites, chromites, manganites, Ni-YSZ cermet, zirconates, doped ceria, hexa-aluminates, pyrochlores, and oxide phosphors, among others. An amino acid such as glycine is commonly used as the fuel in the combustion process. However, urea, citric acid, oxylydihydrazide, and sucrose have also been recently utilized as complexing agents and fuel in the combustion synthesis (9,10).

A simple solution-combustion process is an attractive synthetic route particularly for the preparation of multicomponent oxide materials, since the homogeneity of the aqueous solution of the salts is preserved in the combustion residue. This process is also unique as all the reactants are mixed in solution at the molecular level resulting in homogeneous reaction products and faster reaction rates (9-13).

In the present work, strontium-doped praseodymium manganite ($Pr_{1-x}Sr_xMnO_{3\pm\delta}$ - PSM) and strontium-doped neodymium manganite ($Nd_{1-x}Sr_xMnO_{3\pm\delta}$ - NSM), both with $x \approx 0.3$, cathode powders were synthesized using the urea-nitrate solution-combustion technique (4-6) because of its high-energy efficiency, fast heating rates, short reaction times, and high reaction temperatures. The objective of this study was to synthesize fine powders of PSM and NSM compositions for future preparation of ceramic suspensions for applications as ITSOFC alternative cathodes.

Development of crystalline phases in the powders in different molar relations oxidant-fuel (nitrates salts-urea), was followed by powder X-ray diffraction (XRD). Chemical composition was characterized by X-ray fluorescence spectroscopy (XRF), particle size by laser scattering, surface specific area by gas adsorption and morphology of the powders by scanning electron microscopy (SEM).

EXPERIMENTAL

Powder synthesis

The manganite-based ceramics were synthesized by combustion reactions by employed Aldrich hydrate nitrate salts, $Pr(NO_3)_3 \cdot 6H_2O$ (99.9% purity) and $Nd(NO_3)_3 \cdot 6H_2O$ (99.9% purity), Vetec nitrate salt $Sr(NO_3)_2 \cdot$(99% purity) and Fluka nitrate salt $Mn(NO_3)_2 \cdot 4H_2O$ (99% purity) as cation precursors, and Caal urea, $CO(NH_2)_2$, used as fuel. Distilled water was used for the preparation of solutions. The flow chart for the process is shown in Figure 1.

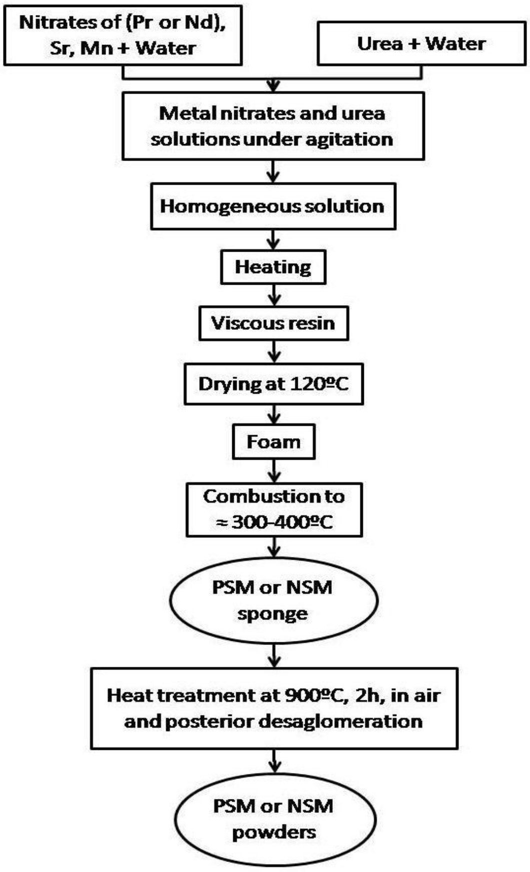


Figure 1: Flow chart for combustion synthesis of PSM and NSM powders.

The stoichiometric composition of each mixture was calculated based on the total oxidizing and reducing valences of the oxidant and the fuel, in order to release the maximum energy for the reaction.

Metal nitrates are employed both as metal precursors and oxidizing agents. Stoichiometric amounts of the metal nitrates, to yield 10 g of the final PSM or NSM oxide powder, were dissolved in distilled water. The urea solution was slowly added to the metal nitrate aqueous solution under constant agitation. Urea acts as a complexing agent for metal cation of varying sizes as it has a carboxylic group at one end and an amino group at the other end. The complexation process increases the solubility of metal ions and helps to maintain homogeneity by preventing their selective precipitation. The water in the solution quickly evaporated the resulting viscous liquid swelled, auto-ignited and initiated a highly exothermic self-contained combustion process, converting the precursor materials into fine powder of the complex oxides. Urea acts as a fuel during the combustion reaction, being oxidized by the nitrate ions. Oxygen from air does not play an important role during the combustion process. The overall combustion reactions can be represented as:

$$0.70Pr(NO_3)_3 + 0.30Sr(NO_3)_2 + Mn(NO_3)_2 + CO(NH_2)_2 \rightarrow$$
$$Pr_{0.70}Sr_{0.30}MnO_{3\pm\delta} + CO_2\uparrow + N_2\uparrow + H_2O$$

$$0.70Nd(NO_3)_3 + 0.30Sr(NO_3)_2 + Mn(NO_3)_2 + CO(NH_2)_2 \rightarrow$$
$$Nd_{0.70}Sr_{0.30}MnO_{3\pm\delta} + CO_2\uparrow + N_2\uparrow + H_2O$$

The presented reactions indicate the formation of CO_2, N_2, and H_2O as the gaseous products. The evolution of gases during the combustion process helps in the formation of fine ceramic powder by limiting the inter-particle contact. The resulting black powder contained some carbon residue and was further calcined to convert to the desired product.

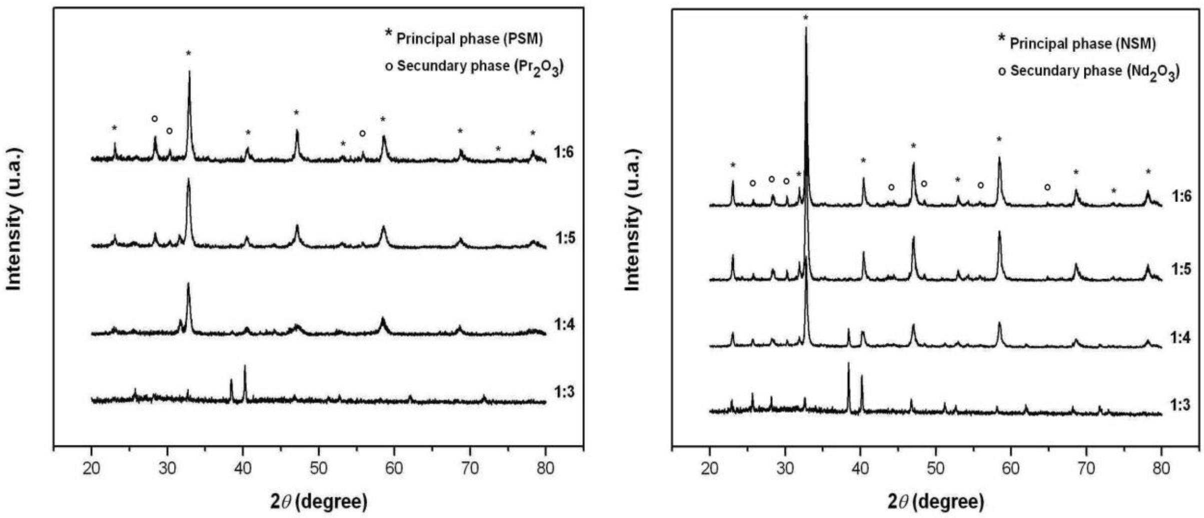
The final treatments were calcination at 900 ºC for 2 hours in air in order to increase the powder crystalline, to reduce carbon residue and attrition-milling for 2 hours using inferior the 1 mm diameter zirconia balls in ethylic alcohol. A final sieve through before characterization was performed. The experiments are directed for compounds attainment for x equal 30 mol % Sr.

Characterization

X-ray diffraction analysis was carried out on powders in different molar relations oxidant-fuel (nitrates salts-urea) for crystalline phase identification. Powder XRD patterns were recorded at room temperature using a step scan procedure (0.02º / 2θ step, time per step 0.5 or 1 s) in the 2θ range 20-80º on a Rigaku Multiflex automated diffractometer equipped with a crystal monochromator employing CuKα radiation. X-ray fluorescence spectroscopy was determined using a Shimadzu EDX900HS. The average agglomerate size was measured by means of a particle-size laser analyzer provided using a CILAS 1064. Specific surface area of the powders was determined using a Micromeritics Analyzer 1330. Finally, agglomerate morphology was observed using a Philips XL30 scanning electron microscope.

RESULTS AND DISCUSSION

The calculation based on principles of propellant chemistry shows urea is required for the combustion; Pr or Nd, Sr, and Mn nitrate mixture for formation of PSM or NSM $^{(14)}$. However, XRD analysis (Figure 2) of the powders obtained after combustion shows phase perovskite formation for ions: urea mole ratio 1:5.



(a) (b)

Figure 2: XRD pattern of powders obtained at various PSM(a) and NSM(b) ions: urea mole ratios (1:3; 1:4; 1:5 and 1:6) showing phase pure PSM formation at 1:5.

In combustion synthesis metal nitrate-fuel mixture is heated between 300 º and 400 ºC to initiate the combustion reaction. In auto ignition process the metal nitrate-urea mixture is first heated in hot plate and the resulting charred powder is then heated in muffle furnace at 900 ºC for removal of carbon and for formation of the crystalline phase. The combustion synthesis process also produced amorphous powders and required further calcinations for pure phase formation.

The Pr or Nd and Sr concentrations used in this study were expected to result in an orthorhombic pseudo-perovskite structure. The Table I present the results obtained by X-ray diffraction. A comparison of our results against those reported by Kostogloudis et al. $^{(6)}$ confirmed the formation of an orthorhombic pseudo-perovskite structure and presence of a small amount of praseodymium oxide (Pr_2O_3) and neodymium oxide (Nd_2O_3).

Table I: Crystalline structure sand lattices of synthesized powder.

Powder	Crystalline Structure	Lattice parameters (Å)		
		a	b	c
PSM	Orthorhombic	5.4860	5.4670	7.7130
NSM	Orthorhombic	5.4494	5.4547	7.9640

The lattice parameters were calculated with Crystallographica Search Match program, which enabled us to find the lattice parameters using the existing JCPDS database for these materials, with their respective crystalline structures and spatial groups. The CELREF program was used to calculate the refinement of the lattice parameters of samples PSM and NSM. The samples showed the presence of a small amount of Pr_2O_3 (JCPDS number 000-81-0820) and Nd_2O_3 (JCPDS number 000-86-1531); resulting from the incomplete during combustion reaction.

The presence of Pr^{3+} or Nd^{3+} in the form of Pr_2O_3 or Nd_2O_3 is influenced by the ionic radius of the ion. The Pr^{3+} ion has an ionic radius of 0.990 Å and Nd^{3+} ion has an ionic radius of 0.983 Å, while the ionic radius of the Sr^{2+} ion is 1.180 Å. Because the ionic radius of the Sr^{2+} ion is larger that Pr^{3+} or Nd^{3+} ions, there is a limitation and substitution these ions for Sr in the structures (15).

The Figure 3 show the spectrum obtained by XRD of PSM and NSM powders after calcination, where it proves the importance of calcination stage for secondary stage elimination and attainment of PSM and NSM pure phase.

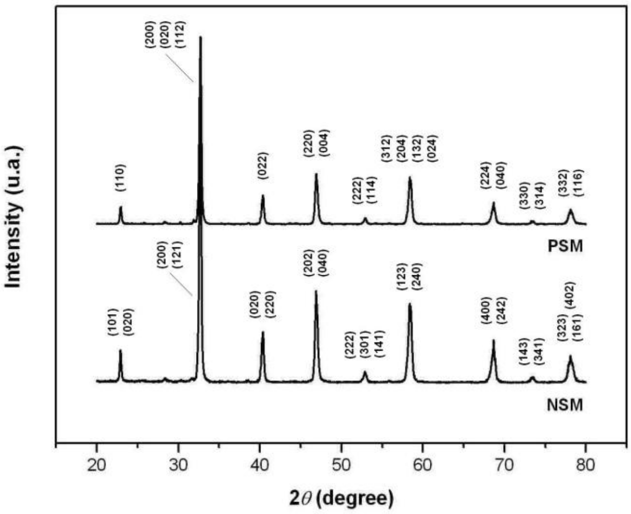


Figure 3: XRD pattern of PSM and NSM powders after calcination.

The results of X-ray fluorescence spectrometry (XRF) were determined the molar values of constituent elements of PSM and NSM powders. The concentrations values of the constituent elements of initial composition are similar with values of synthesized composition obtained in this synthesis, as show in Table II.

Table II: X-ray fluorescence spectroscopy of PSM and NSM samples.

Sample	Stoichiometric composition	Chemical elements (Mass %)	Obtained composition
PSM	$Pr_{0.70}Sr_{0.30}MnO_{3\pm\delta}$	Pr = 34.975 ± 0.078 Sr = 10.777 ± 0.014 MnO_3 = 54,249 ± 0,075	$Pr_{0.67}Sr_{0.33}MnO_{3\pm\delta}$
NSM	$Nd_{0.70}Sr_{0.30}MnO_{3\pm\delta}$	Nd = 37.245 ± 0.074 Sr = 9.799 ± 0.013 MnO_3 = 52.956 ± 0.080	$Nd_{0.69}Sr_{0.31}MnO_{3\pm\delta}$

The powders processed by attrition-milling of the ashes obtained at PSM or NSM ions: urea mole ratio 1:5 show almost same particle size distributions. The particle size observed is in the range 0.2-0.8 µm. The average diameter equivalent (D_{50}) values of the powders are in the range from 0.25 at NSM and 0.27 µm at PSM. Only small fraction (< 10%) of particle is having size higher than 0.20 µm. The Figure 4 shows the equivalent average diameter of PSM and NSM powder prepared at ions: urea mole ratio 1:5.

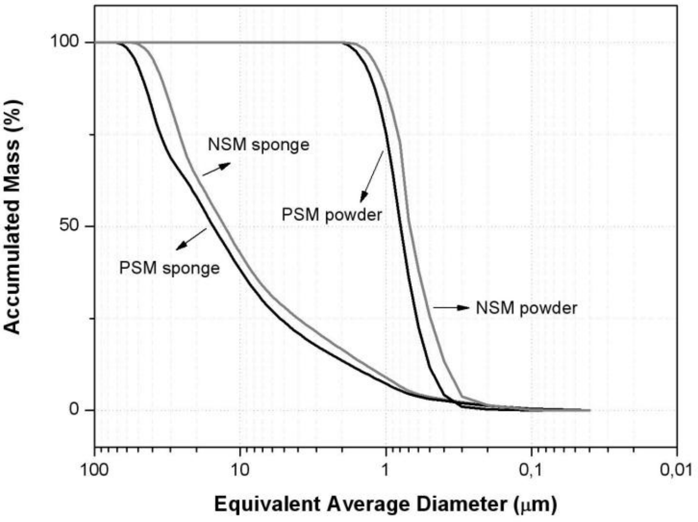


Figure 4: Equivalent average diameter of PSM and NSM samples without milling.

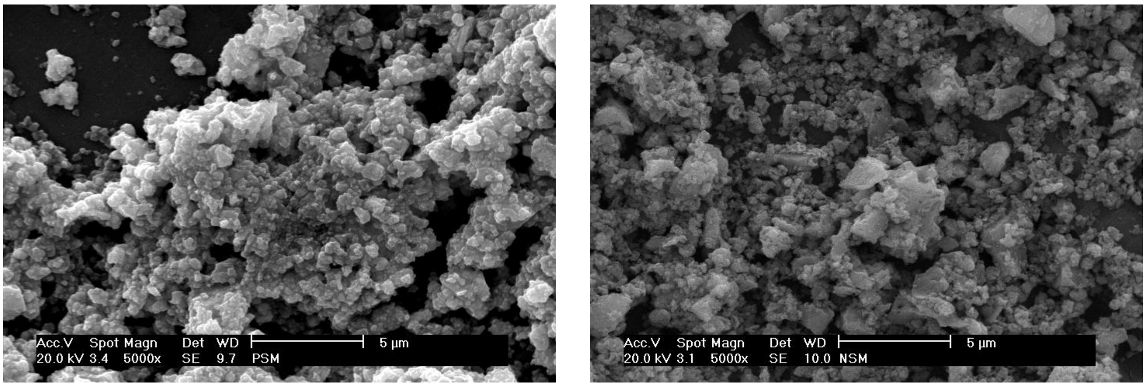
According to Figure 4, after the sponge desaglomeration in mortar, PSM and NSM powders acquires equivalent average diameter inferior at 1 µm. With accomplishment attrition-milling for 2 hours, the particle size if reduces at 0.25 µm.

Grinding for more 2 hours, the particle size if reduces at 0.07 µm (70 nm). Millings above of 4 hours do not intervene significantly with the results. Table III show the equivalent average diameter of PSM and NSM powder prepared after the synthesis and milling stages.

Table III: Equivalent average diameter of PSM and NSM samples.

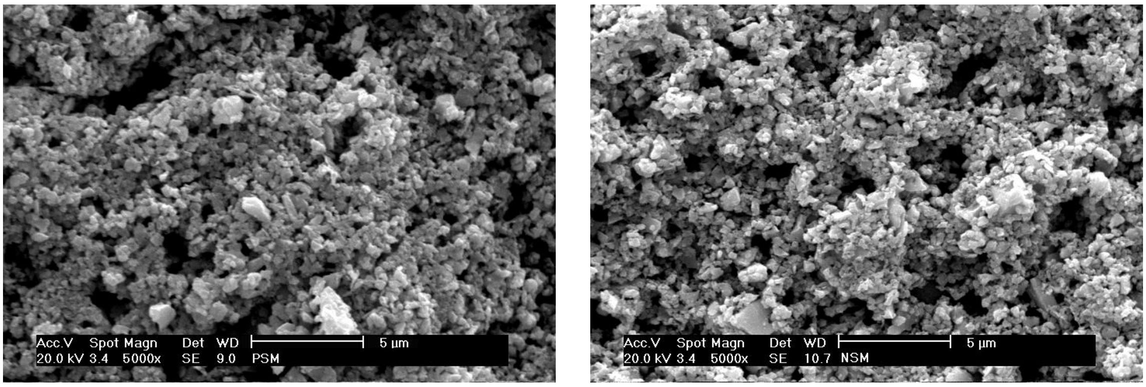
Sample	**Equivalent Average Diameter (µm)**			
	without milling		powder after milling	
	sponge	powder	2 hours	4 hours
PSM	20.54	0.79	0.27	0.08
NSM	15.85	0.67	0.25	0.07

In analysis by SEM were observed the particles morphology of PSM and NSM powders in agglomerates form with the particle sizes inferior at 1 µm (Figure 5) and inferior at 0.5 µm (Figure 6) where homogeneous particles are presented.



(a) (b)

Figure 5: Scanning electron micrograph of PSM(a) and NSM(b) powders obtained by solution-combustion method.



(a) (b)

Figure 6: Scanning electron micrograph of PSM(a) and NSM(b) powders obtained by solution-combustion method after milling of 2 hours.

CONCLUSIONS

Powders of PSM and NSM cathode materials for intermediate temperature solid oxide fuel cells have been synthesized by the urea-nitrate solution-combustion method. Formation of crystalline phases in both the powders started at relatively low temperatures. However, the as synthesized powders had to be calcined at or above 900 ºC and milling to yield phase-pure perovskite products. The analyses by XRF had shown that the synthesis was efficient in the attainment of compositions PSM and NSM, with values around calculated stoichiometric. The scanning electron micrograph had shown that the particle sizes are in the form of agglomerates between 1-0.5 µm. The PSM and NSM powders were observed by XRD, presenting the formation of a main phase with ions: urea mole ratio 1:5 and identification of orthorhombic crystalline structure.

The powders with the particle average sizes inferior at 1 µm are homogeneous particles that can be conveniently used by wet powder spraying on electrolyte substrate. Multiple coatings are necessary to increase the film thickness until 40-50 µm that is thickness adequate as cathode (air electrode).

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