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Solution combustion synthesis of nano particle $La_{0.9}Sr_{0.1}MnO_3$ powder by a unique oxidant-fuel combination and its characterization

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Strontium-doped Lanthanum manganite ($Li_{1-x}Sr_xMnO3$) is the most used cathode material in modern Solid Oxide Fuel Cells (SOFC). A large quantity of LSM is required for making MW scale SOFC units. Many methods of preparation has been reported by various researchers. These include amorphous citrate process, freeze drying, spray pyrolysis, sol-gel, glycine nitrate method and self propagating high temperature synthesis etc. In this paper, a solution combustion synthesis method has been described using a unique combination of oxidant and fuel, nitrate-acetate stoichiometrically, which not only produces nano particle LSM powder but is safe even in large scale production due to gradual combustion without causing any fire hazard or explosion condition which is usually found in most of the solution combustion synthesis reactions. The powder obtained in this method has been characterized by XRD, SEM, particle size analysis, surface area analysis etc. The results have been found to be quite good and suitable for SOFC application. This powder has also been used in forming tubular structure as a part of preliminary experiments to make solid oxide fuel small cell.

1. Introduction

Solid Oxide Fuel Cells (SOFCs) need large quantities of Strontium-doped lanthanum manganite (LSM) as cathode material in modern high capacity cell units. For each kilowatt of power generation about 4.5 kg of LSM is required. Thus for a MW scale power generation unit the quantity of LSM needed is about 4.5 tons. The high price of LSM produced by different methods contributes in a major way to the high cost of SOFC units. So if the cost of production of LSM can be reduced it will have a major impact to the cost of SOFCs.

Different methods tried out by various workers for production of LSM are Pechini method [1], freeze-drying [2], spray pyrolysis [3–5], sol-gel [5, 6], glycine-nitrate method [7] and self propagating high-temperature synthesis (SHS) method [8] etc. In Pechini method which is also known as amorphous citrate method, citric acid/ethylene glycol solution is used to dissolve metal salts followed by evaporation of solvent and decomposition of the residue to get the metal oxide. In freeze-drying process, metals are dissolved in nitric acid when LaMnOs powder of high surface area 14–32 m^2/g is obtained by spraying the solution in liquid nitrogen. For spray pyrolysis, aqueous solutions of metal nitrates are sprayed in a hot pyrolytic chamber specially designed for the purpose for adequate atomization of the solution so that the atomized droplets are decomposed during its flight or/and coming in contact to the hot chamber walls by efficient heat transfer mechanism. In sol-gel method, a precursor, e.g., alkoxide is made to form a gel which on drying followed by decomposition produces the oxide powder. The alkoxide can be made by different techniques, e.g., ammonia method [9]. Glycine-nitrate method is basically a solution combustion synthesis process. SHS method consists of intimate mixing of solid powders followed by pressing it to form pellets. The pellets are ignited at one end to start combustion which then propagates through the pellets releasing heat to form the desired product.

In Pechini method the use of solvent, its evaporation and energy requirement from external source for decomposition adds to the cost to the process. For large scale operation handling organic solvent at elevated tempera-

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ture is not safe due to fire hazard if adequate precautions are not taken. In freeze drying use of liquid nitrogen and spray technique makes the process complicated and as a result the cost of production also goes up. Designing a thermal insulation system for large scale production for minimizing the lose of nitrogen avoiding temperature rise is also not easy. In spray pyrolysis the cost of pyrolytic system which consists of an atomizer, a heat transfer system along with the cost of external heat source is not that attractive. Sol-gel process is a multistage process involving preparation of precursor. Further, cost of organic solvent, maintaining low temperature, e.g., 5°C in ammonia method [9] adds to the complexity and cost of the process. Though it has been claimed that SHS method has different advantages like high productivity, low external energy consumption and use of simple production facilities [8], but it is a lengthy process.

In this paper, a solution combustion synthesis technique is described using a unique combination of oxidant and fuel which has been found very safe, when used stoichiometrically, even in bulk production unlike other fuel-nitrate combinations. LSM produced by this method has been nano particle powder with all desired properties for SOFC application.

2. Experimental system and procedure

The chemicals used for carrying out the combustion reaction were lanthanum oxide (99.9%) from Indian Rare Earths (IRE) whereas nitric acid, manganese acetate and strontium carbonate were E. Merck made analytical reagents. Lanthanum oxide and strontium carbonate were dissolved in dilute nitric acid to make corresponding nitrates at a molar ratio of lanthanum: strontium equal to 9:1. To this solution, aqueous solution of manganese acetate was added so that the nitrate and acetate (oxidant and fuel) forms a stoichiometric mixture for combustion reaction to occur. This solution was heated at 80°C on a hot plate to evaporate water till a viscous gel was formed. After gel formation the temperature of the mixture was allowed to rise so that ignition point of the combustion reaction is reached. It was found that ignition commenced at a temperature below 200°C and slowly progressed till completion when black powder of LSM was obtained. During the reaction gas evolution took place which caused swelling of the reaction mass. However, there was no vigorous flame or explosive condition at any stage of the reaction. The powder so obtained was heated further to 600°C to oxidize any carbon particles present in the mixture and also to allow amorphous LSM to crystallize.

Characterization of this LSM powder was done by XRD using a Philips X-ray diffractometer, model PW 197. Shape, size and distribution pattern of the powders were found out by SEM (model: Philips XL series SEM/EDX XL 30 ESEM) and Horiba LA-500 model, Japanese particle size analyzer. The surface area analysis of LSM powder was carried out by the standard BET technique with NI absorption using a Sorptomatic 1990 CE instrument.

3. Shape formation using LSM powder and porosity development

The LSM powder obtained by above mentioned combustion synthesis was mixed with graphite powder in different proportion. The mixing was done in a polythene container on a roller mill for 2 h. The mixed powders were pressed to form 25 mm diameter pellets at a compaction pressure of 60 Mpa using uni-directional hydraulic press. Sintering was performed in air at 130°C for 2 h after reaching the temperature with the average heating rate of 5°C per minute. The percent porosity of the pellets was calculated from sintered density. The sintered densities were measured by Archimedes Principle.

The same LSM powder was also used to form green tubes by cold isostatic pressing (CIP). These green tubes were sintered at 1300°C for 2 h. The extent of shrinkage was studied in order to achieve final size.

4. Results and discussion

Solution combustion synthesis method has clear advantages over other methods deficiencies of which have been described earlier in this paper. Glycine-nitrate method is essentially a solution combustion synthesis method but due to fire hazard and explosive nature of the reaction it can not be done in bulk scale without specially designed reactor [10]. SHS method needs heating up to 1400°C temperature for 3 h for homogenization and the average particle size is 10 μm only where as in the nitrate-acetate solution combustion synthesis method described above the particle size is in nano meter as has been confirmed by calculating the crystallite size using the Scherrer's formula [11]: $D = 0.9\ \lambda/\beta\ \cos\theta$, where D is the crystallite size in nm, λ, is the wave length of X-ray used in nm, 6 is the peak angle in degree for which full width half maxima (FWHM) taken and P peak broadening at FWHM in radian. The crystallite size estimated from X-ray line broadening of the (110) peak (max. intensity peak) of Fig. 3 was 12 nm.

The particle size distribution patterns of LSM as produced by nitrate-acetate method and graphite powder used as fugitive to make LSM porous body are shown in Figs 6 and 7 respectively. The size of the LSM particles shown in the Fig. 6 is in micro meter. But these particles were agglomerates which were found to break further and further to sub-micron level with more and more powerful ultra sonic de-agglomeration techniques. Particles, which are fundamentally of micron size, can not form sub-micron particles by ultra sonic treatments. Crystallites are small crystals to which a material, possibly, can be de-agglomerated if proper technique is available. So the aforesaid crystallite size, 12 nm of LSM powder indicates that the fundamental size of this powder particles are of nano meter scale only and nano size particles can be formed from it if the powder could be efficiently de-agglomerated. However, TEM was not done for this LSM powder sample.

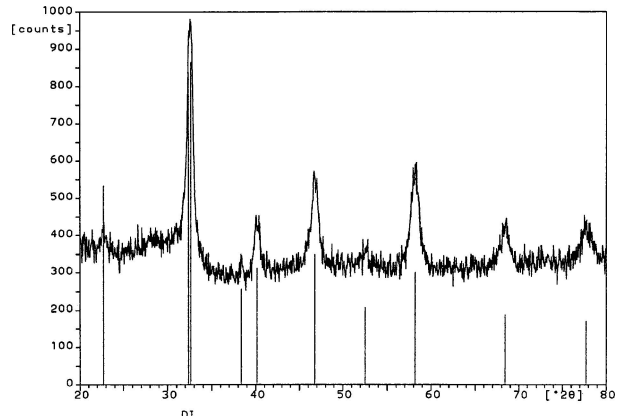

Figure 1 XRD pattern of LSM powder as produced.

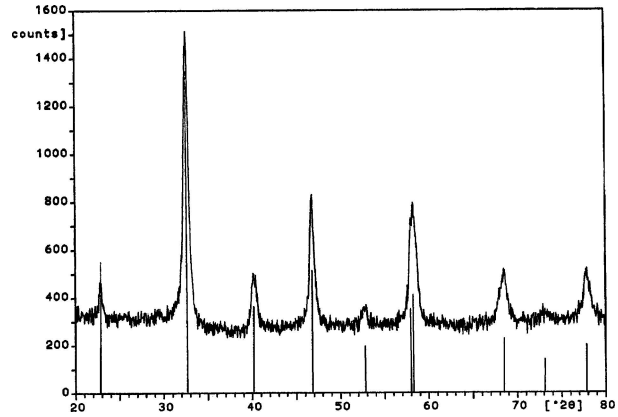

Figure 2 XRD pattern of LSM powder calcined at 600°C.

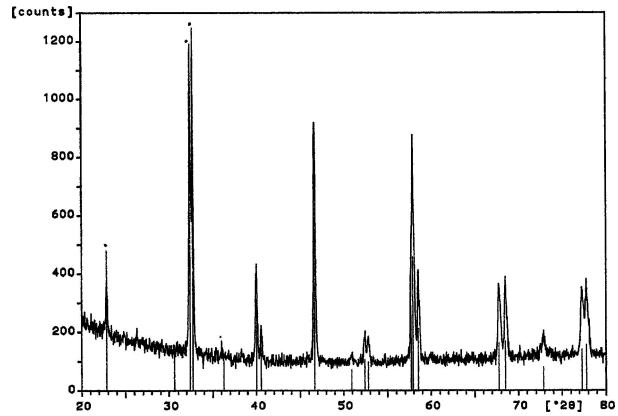

Figure 3 XRD pattern of LSM powder calcined at 1300°C.

The XRD pattern of the LSM powder as produced by this method, calcined at 600 °C and at 1300 °C are shown in Figs 1–3 respectively. These figures confirms the formation of LSM phase and indicate that with the heating at the higher temperatures the powder has become more and more crystalline.

The morphology of the LSM powder produced by nitrate-acetate method in the present work and its porous sintered pellets were studied by SEM. The Figs 4 and 5 shows the SEM images of the powder as produced and the

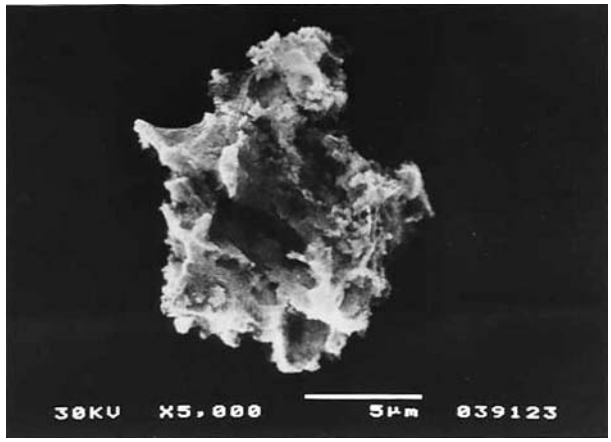

Figure 4 SEM image of LSM powder as produced by nitrate-acetate method.

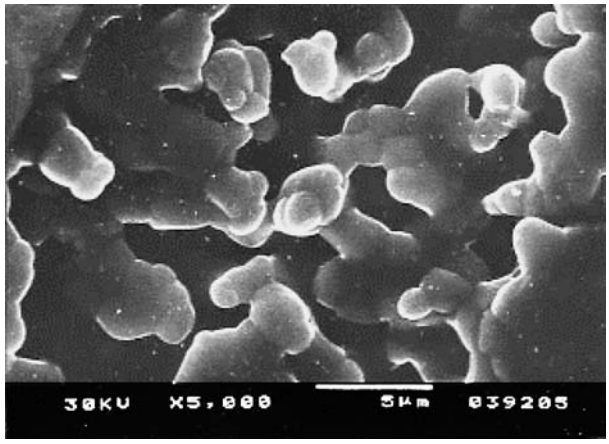

Figure 5 SEM image of LSM porous pellet from powder of nitrate-acetate method obtained by sintering at 1300°C.

40% porous LSM pellet sintered at 1300°C respectively. While the in Fig. 4 LSM powder appears as a solid lump, in Fig. 5 wide pores are clearly visible.

The Table I shows the weight percent of graphite added as pore former to LSM powder and the corresponding porosity obtained in sintered LSM body. The table shows that increase is percent of pore former increases the percent porosity in LSM body. The 40% porosity was obtained using 35% weight fraction of the graphite. Fig. 5 shows the micrograph of 40% porous LSM body. The micrograph confirms the uniform distribution of porosity. The open porosity was measured by using modified

TABLE I Porosity of LSM sintered pellet with respect to percent of fugitive used

Weight% Graphite	25.45	34	**35**	44
Sintered density	65	57	**55**	45
Porosity	35	43	**45**	55
Open porosity	28	38	**40**	52

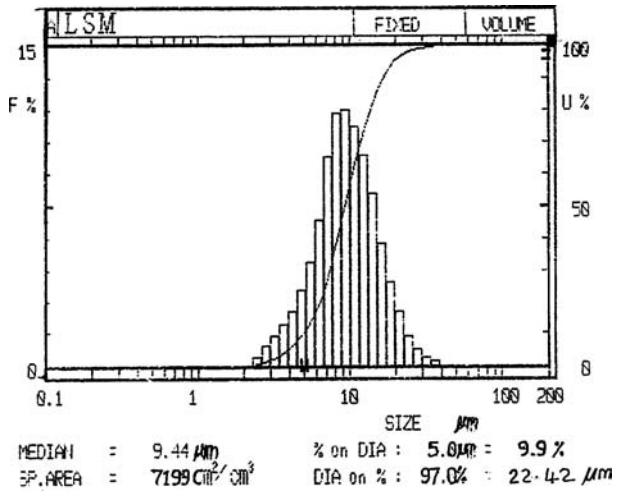

Figure 6 Particle size distribution of LSM powder as produced by nitrate-acetate method.

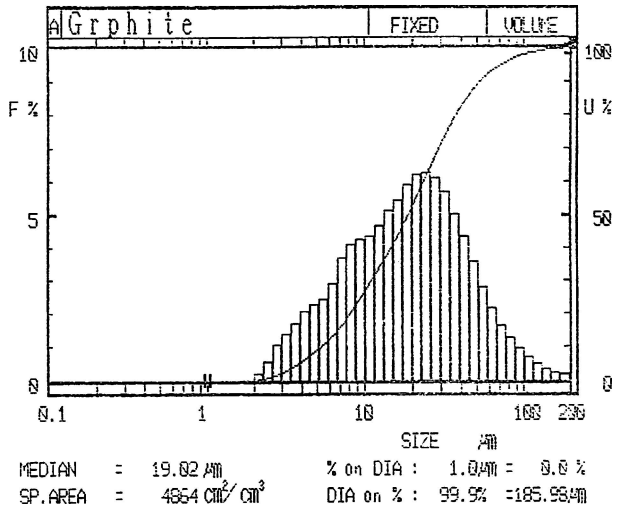

Figure 7 Particle size distribution of graphite powder used as fugitive.

Archimedes formula:

$$\text{Open porosity} = \frac{W_3 - W_1}{W_3 - W_2}$$

where W_1 = Weight of pellet in air, W_2 = Weight of pellet in water, W_3 = Weight of wet pellet in air.

Specific surface area (S_{BET}) of the calcined powder was 86.17 m^2/g. The equivalent spherical diameter (D_{BET}) was calculated using the formula: $D_{BET} = 6/\rho S_{BET}$, where ρ is the theoretical density of the powder (6.6 g/cc). Equivalent spherical diameter calculated from specific area data was found to be 10.5 nm.

Trial runs were taken to study the extent of shrinkage of the green LSM tube obtained by cold isostatic pressing during sintering process. Based on this information the initial size of the green tube could be chosen/made in order to get the desired final size of the sintered tube.

Some researchers in recent works [12, 13] have applied coextrusion of multiple pastes containing a water-based binder for making tubular anode/electrolyte two-layer ceramic composites.

The LSM powder was produced in kilogram quantities by the nitrate-acetate method in a batch size of 250 g each. This solution combustion synthesis was found to be absolutely safe from any fire or explosion point of view. The chemicals used were cheap and the energy requirement was low due to auto ignition taking place during the reaction which itself provided a major portion of the required heat to carry out the process. Unlike other methods solution combustion synthesis method can be applied to produce many other oxides e.g., new anode materials like doped lanthanum chromites for SOFC [14] etc.

5. Conclusions

The nitrate-acetate method of solution combustion synthesis of LSM is cheaper than other methods. It is safe for producing the powder in large scale. The powder produced by this method has been found to be of nano particle size. Using graphite as a fugitive, 40% porous body of LSM could be made which is required to use this powder as cathode material in SOFC. The powder produced by the nitrate-acetate method could be successfully used to form tubular shape of pre-determined size by cold isostatic pressing followed by sintering.

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