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Synthesis and processing of lanthanum strontium manganite ($La_{0.84}Sr_{0.16}MnO_3$) powder by co-precipitation technique

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Lanthanum strontium manganite ($La_{0.84}Sr_{0.16}MnO_3$-LSM) bodies in the form of tape, tube and coating with desired amount of porosity find application as cathode material in electrode or electrolyte supported designs of solid oxide fuel cells (SOFC). Formation of these bodies by solution-based fabrication techniques such as tape casting, slip casting, extrusion and screen-printing requires powder possessing desired characteristics. There are various methods reported for formation of the powder such as solid state reaction, sol-gel, solution combustion, co-precipitation [1–7]. In preparing powders by any such methods the important aspects to be studied are formation of the phase pure LSM compound of desired chemical composition and tailoring of the powder characteristics to make it suitable for the fabrication technique. In precipitating precursor for formation of multi-metal oxide system, reverse strike precipitation ensures the simultaneous co-precipitation of all the different metal ions to provide uniform mixing. A study of the thermal decomposition and phase evolution behavior of the precursor by TG-DTA and XRD techniques is important from the point of view of fixing the calcination condition to form the phase pure compound. As the oxide powder formed by calcination always contains coarse agglomerates that can introduce micro-structural heterogeneities in the bodies formed, they need to be eliminated by wet grinding. One precondition for effective wet grinding is that the individual particles should remain dispersed during the process (both initial agglomerates and the particles formed by grinding). Dispersion behavior is evaluated through zeta-potential and viscosity (influenced by pH and solid content) studies on the slurries [8]. Grinding behavior is evaluated through particle size distribution data. Also a study of the role of calcination temperature on the dispersion, grinding and solid loading behavior of the powder throws light on the optimum conditions to form the powder with desired characteristics. As no such study has been reported on the formation of a carbonate precursor by reverse strike co-precipitation and its processing to form into phase pure LSM ($La_{0.84}Sr_{0.16}MnO_3$) powder with desired powder characteristics, it was carried out in this laboratory and the results are presented in this paper.

The precursor was co-precipitated by drop wise addition of an aqueous solution of lanthanum nitrate, manganese nitrate and strontium nitrate (total metal ion concentration of the solution was ~0.15 M) to a bath of ammonium carbonate (~0.15 M) kept vigorously stirred (batch size ~50 g of LSM). Total amount of ammonium carbonate used was about 1.5 times of that required, to ensure its presence in sufficient concentration throughout the course of precipitation. The precipitate was filtered, washed thrice with excess water and finally dried in air oven. Its chemical composition was fixed from estimation of carbonate content by gravimetric method. The powder formed was subjected to thermal decomposition studies by TG-DTA in a thermal analyzer (M/s. Netzsch) and phase evolution by XRD (M/s. Philips). The powders calcined at 1100° and 1350 °C were subjected to dry grinding in a planetary mill (M/s. Fritsch) for 1 h until it formed a cake along the wall of the pot (material of pot and ball: alumina). The zeta-potential variation with pH for the aqueous suspensions was studied using Zetasizer 3000 (M/s. Malvern). Viscosity variation with shear rate for slurries with varying solid concentration was studied using a cone and plate viscometer (M/s. Boehlin). The particle size distribution of the variously wet ground powders was evaluated using Mastersizer 2000 (M/s. Malvern).

The precipitate formed was a granular and was easily processed (i.e., filtered, washed and dried). The chemical composition of the precursor i.e., its empirical formula could be written as $La_{0.84}Sr_{0.16}Mn(CO_3)_{2.10}(OH)_{0.64}\cdot 0.92\,H_2O$ based on the carbonate estimation and TG data.

The thermal decomposition behavior of the precursor is shown in Fig. 1. It exhibited a shallow endotherm accompanied by a loss in weight of about 5 percent in the range of 25 to 200 °C which could be attributed to the loss of absorbed moisture. It was followed by two endothermic processes accompanied by loss in weight in stages (23% loss in weight accompanied by a sharp endotherm in the temperature range of 400 to 600 °C and about 7% loss in weight accompanied by an endotherm in the temperature range of 800 to 900 °C). Pure lanthanum carbonate has been reported to decompose in to an intermediate oxy-carbonate phase in the temperature range of 400 to 600 °C that finally forms into lanthanum oxide in the temperature range of 700 to 900 °C [9]. As reported in hand book of physics and chemistry, manganese carbonate decomposes above 200 °C while pure strontium carbonate decomposes at about 1280 °C.

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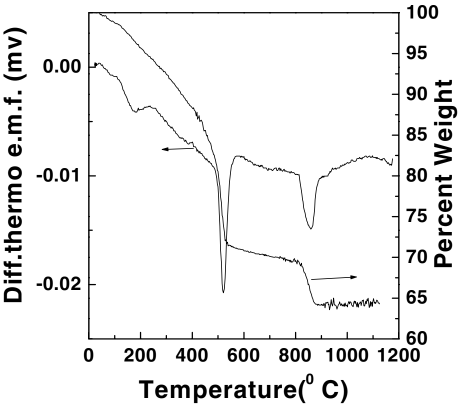

Figure 1 TG-DTA pattern of the precursor (rate of heating: 10 °C/min in air).

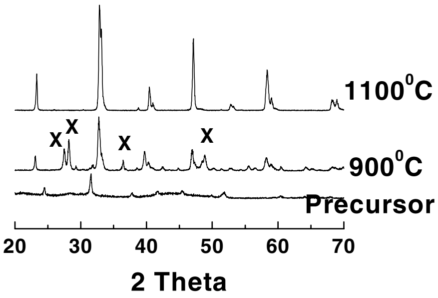

Figure 2 XRD patterns for the precursor heated to 900 ° and 1100 °C (rate of heating: 10 °C/min and quenched) peaks marked as X refer to SrO; unmarked peaks refer to LSM.

The XRD pattern of the precursor, and that heated to 900 and 1100 °C are shown in Fig. 2. The precursor appears to be a mixture of poorly crystalline and amorphous carbonates as shown by the presence of some peaks on the broad pattern. The precursor pattern, even though the precursor decomposed and formed into the oxide compound LSM at 900 °C, revealed the presence of a second phase that could be indexed as strontium oxide (PCPDF No. 82-0915) [10]. Early decomposition of strontium carbonate below the reported 1280 °C could be attributed to its reactivity induced by the presence of lanthanum and manganese oxides. However, the compound heated to 1100 °C exhibited pure LSM pattern (PCPDF No. 40-1100) [11]. Hence the precursor was calcined at 1100 °C for 1 h and subjected to further studies on dispersion and grinding behavior evaluation. To bring out the role of calcination temperature, the precursor calcined at 1350 °C was also subjected to the above studies.

The powders thus formed by calcination at 1100 and 1350 °C were dry ground planetarily for about one hour. As they formed a cake along the wall of the pot in one hour, no further reduction in particle size could be expected by dry grinding. The particle size distributions of both the dry ground powders are shown in Fig. 3A and B. Both the powders possessed similar mean diameter ($D_{50} \sim 6$ μm) and contained substantial amount of agglomerates in the range of 10 to 50 μm. Presence of such agglomerates introduces heterogeneities in the green microstructure and defects in the sintered product. Hence it is essential to get rid off such agglomerates by wet grinding. The optimum dispersion conditions for the slurries of these dry ground powders for wet grinding were obtained from their zeta-potential and viscosity data (i.e., zeta-potential variation with pH and viscosity variation with shear rate).

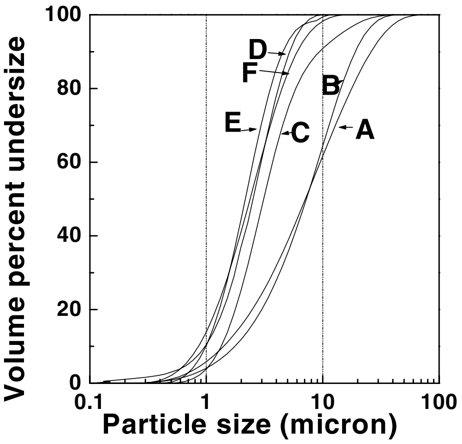

Figure 3 Particle size distribution of dry and wet ground powders: A, B—1100 ° and 1350 °C calcined powders dry ground for 1 h; C, D, E—A wet ground for 4 h with slurry concentrations of 18, 15 and 10 volume percent solid; F—B wet ground for 4 h with slurry concentration of 15 volume percent solid.

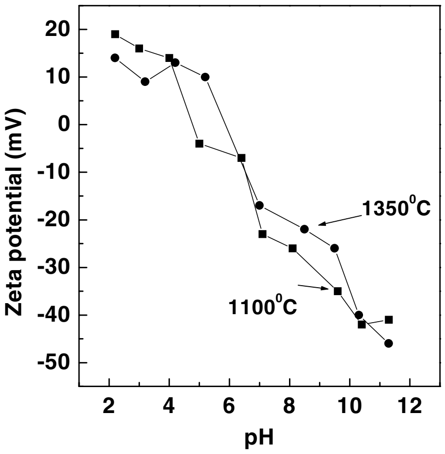

Figure 4 Zeta-potential variation with pH for the aqueous suspensions of LSM powders calcined at 1100 ° and 1350 °C.

Zeta-potential variation with pH for the aqueous suspensions of 1100 ° and 1350 °C calcined powders is shown in Fig. 4. The zeta-potential of the suspensions of both the powders remained essentially the same. The particles are weakly charged in acidic and neutral solutions (<15 mV) but well charged in the alkaline pH range of ∼10 to 11 (−35 to −45 mV) for both the powders, establishing presence of a strong columbic barrier of repulsion between particles in this pH range. Thus the dispersions of both the powders are stabilized only in pH range of 10 to 11.

Even at the pH of maximum zeta potential, flocculates are reported to exist in concentrated slurries, which is exhibited in their rheological behavior. The variation of viscosity with shear rate for alkaline slurries (pH ∼10) as a function of the solid concentration for the 1100 and 1350 °C calcined powders is shown in Fig. 5. It is obvious that the slurries from both the calcined powders (in the range of 10 to 30 vol% solid concentration) exhibit shear thinning or pseudo-plastic

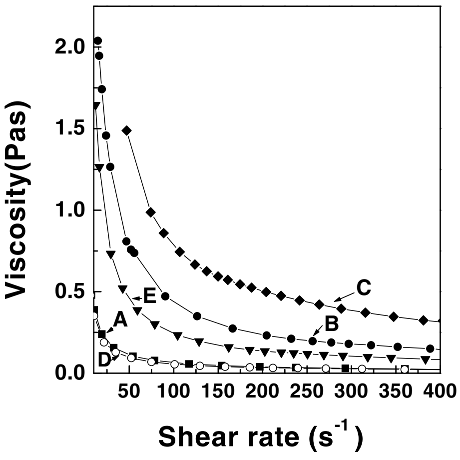

Figure 5 Viscosity versus shear rate plots for slurries from dry ground powders (pH ∼10); A, B, C—slurries with 10, 15 and 18 vol% of 1100 °C calcined powder; D, E— slurry with 15 and 30 volume percent of 1350 °C calcined powder.

flow behavior (i.e., decrease in viscosity with increasing shear rate). For the slurries of both the calcined powders, the shear rate above which the viscosity becomes constant (i.e., Newtonian flow behavior) decreases with decreasing solid content. The flocculates present in slurries entrap water inside their structure thereby making it unavailable for flow and hence increase the viscosity. Upon shearing, the flocculates break and the water become available for flow thereby decreasing the viscosity. Thus the shear thinning behavior is attributed to the breaking away of the flocculates. The shear rate above which viscosity becomes less dependent on it (Newtonian behavior) is a measure of the strength of the flocculates. A decrease in this value with decreasing solid concentration in slurries indicates a decrease in the flocculate strength.

The role of calcination temperature on the viscosity of the slurries of dry ground powders is shown in Fig. 5. For a given solid concentration (e.g., 15 vol% solid loading), slurry of 1350 °C calcined powder exhibits a much lower viscosity than that from 1100 °C calcined powder, indicating improved solid loading (Fig. 5B and D). Generally, calcination at higher temperature reduces the specific surface area due to densification of the individual particles and hence the porosity of the particle. Reduced porosity reduces the amount of water entrapped inside the particle, thereby making it available for decreasing the viscosity. Thus the viscosity of the slurries decreased drastically (i.e., the solid loading behavior increased) with increasing calcination temperature. The grinding behavior was evaluated from the particle size distribution data.

Under a standard set of wet grinding conditions (Table I), the particle size distributions of the ground slurries with varying solid content of the 1100 °C calcined powder showed that the size did not depend on solid content below a concentration of 15 vol% (Fig. 3C, D and E). This showed that the shear rate produced during milling was higher than the critical shear rate above which flocculates cease to exist in the system with 15 vol% solid concentration. Grinding was less efficient for the slurry with 18 volume percent solid concentration indicating the higher strength of the flocculates that do not break by the shear during grinding. Under the same set of grinding conditions, both 1100 ° and 1350 °C calcined powders could be ground to almost the same size ($D_{50} \sim 2.5$ to 3 μm) free of agglomerates with size greater than 10 μm (Fig. 3D and F), exhibiting little difference in their grinding behavior.

TABLE I Mill parameters used for planetary grinding (amount of powder: 30 g)

Type of grinding	Mill (r.p.m)	Pot size (cc)	Ball diameter (mm)	No. of balls	Time (h)
Dry	200	250	20	4	1
Wet	200	80	6	30	4

The feature of decreasing viscosity with increasing calcination temperature was retained in the ground slurries also. Powders exhibiting higher solid loading capability in slurries are desired for shape forming processes, as chances of introduction of defects in the green and sintered products is reduced due to reduction in shrinkage during drying and sintering.

Thus the calcination temperature for preparation of phase pure LSM powder from the carbonate precursor formed using the reverse strike co-precipitation technique has been found to be 1100 °C. Suspensions of both the 1100 and 1350 °C calcined powders were found to exhibit a maximum in zeta-potential value in the pH range of 10 to 11, indicating the ideal pH for dispersion. However the viscosity decreased with increasing calcination temperature (1100 to 1350 °C) for slurries of both dry and wet ground powders (i.e., exhibited improved solid loading behavior with increasing calcination temperature). The grinding behavior of the powders remained essentially the same for both calcined powders. As the powder possessing higher solid loading capacity is desired for solution based shape-forming techniques (tape casting, slip casting, extrusion, screen printing), powder calcined at 1350 °C and ground free of agglomerates is preferred for the above shape forming techniques.

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