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Studies on slip casting behavior of lanthanum strontium manganite

M.B. Kakade [a,*], D. Das [b], S. Ramanathan [a]

[a] *Materials Processing Division, Bhabha Atomic Research Centre, Mumbai 4000 85, India*
[b] *Chemistry Division, Bhabha Atomic Research Centre, Mumbai 4000 85, India*

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Abstract

Dispersion conditions for slip (slurry) formulation of a powder mixture of lanthanum strontium manganite ($La_{0.84}Sr_{0.16}MnO_3$ – LSM) and carbon (pore former) in water was studied through detailed zeta-potential and rheological measurements. The zeta potential variation with pH for the aqueous suspensions of only LSM or carbon exhibited a maximum value in alkaline medium (−40 mV to −50 mV at a pH of 10–11), establishing the pH window for their co-dispersion for slurry formulation. A study of the viscosity variation with shear rate for the slurries with varying solid content (in the range of 45–65 wt.%) exhibited pseudo-plastic flow behavior, indicating presence of flocculates in them. The yield stress values obtained from the Casson equation reduced with decreasing solid content, indicating reduction in the flocculate strength. The slip with solid content of 50 wt.% exhibited optimum flow characteristics to form long tubes with uniform wall thickness (wall thickness 2–4 mm and length of 150–200 mm). The tubular specimens formed after controlled carbon burn out and sintering at 1400 °C for 1 h possessed about 35% open porosity. The porosity remained the same upon further sintering at 1400 °C for 8 h.

Keywords: A. Slip casting; B. Porosity; E. Fuel cells; Lanthanum strontium manganite

1. Introduction

Lanthanum strontium manganite bodies find application as a cathode material in solid oxide fuel cells (SOFCs) [1]. Out of the many designs of the SOFC, the tubular one possess the advantage of not requiring any sealant, voluminous interconnect structures and is built as a relatively separate unit structure [2]. It is easy to replace, assemble cells and built up a generation system in larger scale. In this design, porous LSM tubular bodies act as the support for the dense thin film of the YSZ electrolyte. The dense electrolyte film is formed on the porous tube through electro-vapor deposition (EVD) while lot of research is pursued in developing cost effective electrophoretic deposition (EPD) and dip coating techniques [3–6]. In all these methods for the formation of the dense electrolyte coating free of open porosity, the coated porous tubular body needs to be heated to a temperature in the range of 1300–1400 °C. One of the preconditions for the LSM tubular bodies is that the porous structure should be stable (i.e., should not undergo densification) during its subsequent heating while forming the electrolyte coating. Tubular porous LSM specimens find application in many studies such as formation of the test cells, current–voltage and polarization characteristics, evaluation of their thermal cycling behavior, etc. [7–9].

Tubular bodies can be formed by the standard ceramic fabrication techniques such as extrusion, slip casting, isostatic pressing [1,2,10]. Slip casting is the most versatile technique and possess capability to fabricate products with complex shapes and homogeneous cast composition. The slip characteristics need to be tailored to ensure formation of proper dispersion and is measured by zeta-potential and viscosity studies. Also the slip characteristics should be optimized to make easier the process of exercising control over formation of desired dimensions of the shape. The role of process conditions on the dispersion characteristics of the slip and its casting behavior has been extensively described by Robert Fries and Brian Rand [11]. For materials with higher density (e.g. LSM ~6 g/cc), under a given set of dispersion conditions (i.e., pH and solid concentration), lowering the particle size increases the stability of the slip towards segregation (desirable for producing homogeneous green microstructure). However, retention of porosity after sintering is made difficult (undesir-

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* Corresponding author. Tel.: +91 22 25590466; fax: +91 22 25505151.
E-mail address: mkakade@barc.gov.in (M.B. Kakade).

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able for formation of porous bodies). In liquid based ceramic fabrication techniques, engineered porosity is introduced in the products by incorporating less dense coarser particles of pore former, like carbon in the slurry of the material [12]. In case of LSM, the bodies so obtained should have been sintered at a temperature of about 1400 °C to avoid further sintering of the porous structure during formation of the electrolyte coating (which require subsequent heating to the above temperature).

Hence a detailed investigation on the role of process conditions on the dispersion characteristics of the slip of LSM and carbon (pore former) powders, cast formation and the sintering behavior of the bodies formed was carried out.

2. Experimental

Lanthanum strontium manganite powder with the formula composition of $La_{0.84}Sr_{0.16}MnO_3$ (LSM) was prepared by the combustion reaction of an aqueous solution of metal nitrates (oxidizer) – citric acid (fuel) in desired proportion on a laboratory heater. The combustion reaction can be represented as:

$$\begin{aligned} &0.84\,La(NO_3)_3 + 0.16\,Sr(NO_3)_2 + Mn\,(NO_3)_2 \\ &\quad + 1.36\ C_6H_8O_7 \rightarrow La_{0.84}Sr_{0.16}MnO_3 + 8.16\,CO_2 \\ &\quad + 2.44\ N_2 + 5.44\ H_2O \end{aligned} \tag{1}$$

Thus the stoichiometric molar ratio of citric acid to nitrate ion required is 0.28 while the number of moles of gaseous product evolved per mole of LSM formed is 16.04. The as formed powder was calcined at 1300 °C for 1 h to sinter the individual particles and wet grinding for 1 h to disperse into individual particles. Carbon (petroleum coke) powder was used as the pore former. The particle size distribution of the powders was measured using laser light scattering technique based on the principle of Mie Theory (Master-sizer 2000, M/s. Malvern). The zeta-potential of the aqueous suspensions of only the LSM or carbon powder with varying pHs was evaluated using ‘Laser Doppler Electrophoresis’ (Zeta-sizer 3000, M/s. Malvern) to obtain the optimum pH for the best dispersion of a mixture of both together. A powder mixture of LSM and carbon (weight ratio of 3:1) was used for formulation of aqueous slips with varying solid content and were evaluated for their rheological behavior using a cone and plate viscometer (M/s. Boehlin).

The rheological data was fitted using the Casson model – [$\tau^{1/2} = \tau_y^{1/2} + (K\gamma)^{1/2}$ where ‘τ’ is the shear stress, ‘τ_y’, is Casson yield stress, ‘K’ is Casson viscosity and ‘γ’ is the shear rate] – and the rheological parameters calculated (Table 1). The casting behavior was evaluated in plaster of Paris moulds using slips with varying solid concentration. The time taken for casting to a wall thickness of 2 mm was calculated for slips with varying solid content. All the specimens were heated to 1100 °C slowly (rate of heating 0.5 °C/min) followed by heating to the sintering temperature of 1400 °C (5 °C/min) and soaked up to 8 h. The sintered specimens from slips of different solid content were evaluated for the uniformity of their wall thickness and density (Archimedes method) along the length by measuring the above data on the specimens of about a 2.5 cm obtained by cutting the sintered tube. The micro-structure of the specimens was studied using the scanning electron microscope (M/s. Jeol).

Table 1
Fitted parameters obtained from Casson model for the different slips.

Solid content (wt.%)	Yield stress (Pa)	Viscosity (Pas)	Correlation coefficient
65	26.3	0.41	0.98
60	10.1	0.15	0.99
55	4.6	0.14	0.986
50	3.2	0.11	0.996
45	2.1	0.12	0.999

3. Results and discussion

3.1. Powder treatment

Preparation of LSM compound by the combustion reaction of an aqueous solution of metal nitrates and citric acid has been found to be the most versatile technique while calcination treatment at 1300 °C of the as formed powder has been found to reduce the viscosity of the slip for any given solid concentration due to sintering of the individual particles eliminating the internal pores [13,14]. Hence slip casting behavior of this powder was studied. The particle size distribution of the 1300 °C calcined and 1 h ground LSM powders and that of the carbon (pore former) powders used are shown in Fig. 1. The calcined and ground LSM powders exhibited mean sizes (D_{50}) of 10 and 3.5 μm respectively. The carbon powder exhibited mean size (D_{50}) of 15 μm. Slips stable towards settling during casting could be formed using the powders of these sizes. The requirement of pore size larger than submicron size for the cathode material of SOFC has been emphasized by Tedmon et al. [15]. Generally large pore size in the ceramics is created using carbonaceous fugitives and hence petroleum coke with $D_{50} \sim 15$ μm was used in this study.

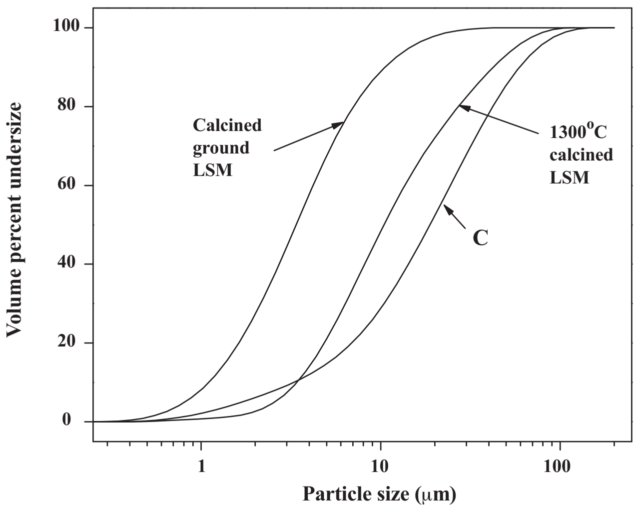

Fig. 1. Particle size distribution of the LSM and pore former (carbon) powders.

3.2. Dispersion behavior

The dispersion of particles in water can be achieved by the electrostatic columbic repulsion mechanism due to presence of adsorbed charge on them [11,16]. During preparation of slip of mixed components (e.g. LSM and carbon powders) it is essential to keep both the particle sufficiently like-charged so that the suspension remains stable. The quantitative parameter used for evaluating the charge on the particles in aqueous suspensions is zeta-potential [17,18]. It is the potential measured at the shear plane when the particle is moved through the liquid. It is a function of powder characteristics, presence of electrolyte ions and pH of the medium.

The zeta-potential variation with pH for the aqueous suspensions of the LSM and carbon powders is shown in Fig. 2. It is obvious that the LSM suspensions exhibit maximum zeta-potential only in alkaline pH ($pH > 10$). It appears that in acidic range the surface chemistry of the LSM particle is such that there is a positive potential. Thus dispersion of LSM powder in aqueous medium is electrostatically stabilized only in alkaline medium and the particles, as expected, are negatively charged. The zeta-potential variation for the carbon powder suspensions in the pH range of 8–11 also exhibited negative charge (maximum value of -55 mV at a $pH \geq 10$). Thus at a pH of 11, both LSM and pore former particles are sufficiently like-charged indicating the optimum pH window for their co-dispersion. Hence slips with varying solid content were prepared at a pH of 11.

3.3. Rheological behavior

Even at the pH of maximum zeta-potential, flocculates are said to be present in the slurries with higher solid loading [17,19,20]. It is exhibited in their rheological behavior. The viscosity versus shear rate plots for the slips with varying solid contents (mixture of LSM and carbon powders in the weight ratio of 3:1; $pH \sim 11$) are shown in Fig. 3. For all the slips, with increasing shear rate, the viscosity decreased gradually and attained a constant value above a critical shear rate (i.e., shear thinning behavior) which is attributed to the breaking away of the flocculates present in slips upon shearing [19]. With decreasing solid content in the slip, the viscosity decreased and the critical shear rate above which viscosity becomes constant also decreased, indicating the flocculates becoming weaker with dilution. The decrease in the yield stress calculated from the Casson plots (Table 1) also confirmed this. Also it is interesting to note that the decrease in viscosity becomes less significant with decreasing solid content in the slip (Fig. 3).

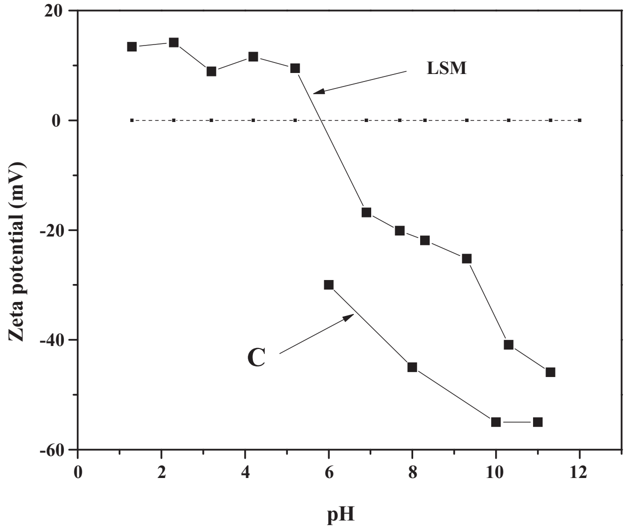

Fig. 2. Zeta-potential variation for aqueous suspensions of LSM, carbon powders with pH.

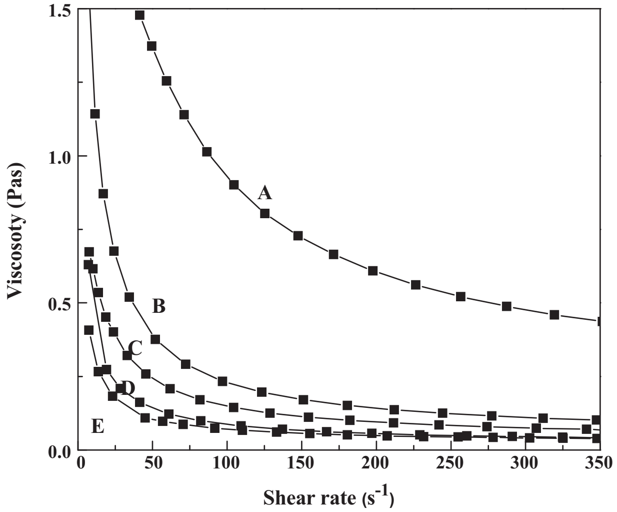

Fig. 3. Viscosity variation with shear rate plots for slips of (LSM + carbon) A, B, C, D, E – slips with of 65, 60, 55, 50 and 45 wt.% solid content in water at a pH of 11.

3.4. Slurry optimization

In any ceramic shape forming method, obtaining a homogeneous green body micro-structure is a precondition for formation of a quality and defect free sintered product. In slip casting, heterogeneity in microstructure results due to segregation and clogging phenomena which occur during liquid removal [21]. Segregation occurs due to higher rates of settling down of particles with larger size and density under the effect of gravity. Clogging effect occurs due to faster moving of finer particles along with suspending medium and it occurs in the direction parallel to that of liquid flow. As the liquid is removed into the pores present in the mould, the particles are dragged into its wall. The finer and lighter ones move faster towards the wall due to lesser inertia while the coarser ones form the subsequent layers of the wall, resulting in heterogeneous microstructure. These problems can be minimized by: (a) increasing the viscosity of the slurries using higher solid content in the slips; and (b) increasing the rate of cast formation i.e., reducing casting time. However, higher viscosity of the slip could result in improper mixing of the components during slip formulation, entrapment of air bubbles in the cast and formation of non-uniform cast thickness. Non-uniform wall thickness of the tube from bottom to top can result due to reduced time of

Table 2
Slip concentration versus casting time for forming a wall thickness of 3 mm.

Slip concentration (wt.%)	Time of casting (min)
65	Could not be measured
60	Could not be measured
55	2
50	5
45	9

casting compared to the time taken for filling and draining of the mould in case of very concentrated slips. Also defects get introduced due to improper flow of the slip into the interior details of the mould. Thus it is essential to optimize the rheological parameters of the slurry to form quality casts with homogeneous microstructure and it varies with product dimensions. For long one closed tubular specimens, it is done from the following points of view: (a) the slip should easily flow into and drain out the mould, and the time taken for the above should be much less compared to the time of casting to ensure uniform wall thickness; and (b) avoid segregation of particles due to gravity and clogging effects during the course of the process. The slip with a solid concentration of 50 wt.% was found to be the ideal one for forming tubes with wall thickness in the range of 2–4 mm. The variation in the time taken for formation of a given wall thickness ($\sim$2 mm) by slips with varying solid content is found to be strongly influenced by the solid content (Table 2).

3.5. Casting process

The casting process to form tubular specimen with a uniform wall thickness of about 2–4 mm and length of 150–200 mm could be finished in about 10 min using the slurry with solid content of 50 wt.%. The bodies after drain casting were dried in the mould for about 2 h to form into a rigid shape, which could subsequently come out of the mould easily. These bodies were air dried in ambient atmosphere for slow evaporation of residual moisture to avoid introduction of cracks. They were subsequently subjected to control burning out of the carbon particles (pore former) by heating at 0.5 °C/min up to 1100 °C. Controlled rate of heating enabled slow evolution of gases resulting in formation of crack-free bodies. These bodies sintered at 1400 °C from 1 to 8 h exhibited same bulk density and open porosity (65% T.D. and 35% open porosity) as estimated by the water immersion technique. The photograph of the slip cast LSM tubes sintered at 1400 °C is shown in Fig. 4. The wall thickness and density/porosity data of the sintered bodies cut at different lengths exhibited little variation showing the absence of heterogeneity due to segregation of particles.

Fig. 4. Typical slip cast LSM tubes sintered at 1400 °C.

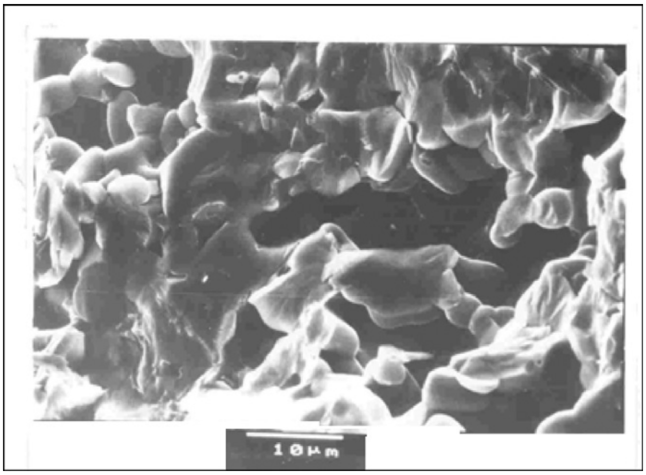

Fig. 5. Typical SEM micrograph of the porous LSM slip cast tube sintered at 1400 °C.

3.6. Microstructural evaluation

The porous morphology of the sintered porous tube is shown in Fig. 5. Straight tubes with uniform wall thickness have been obtained. The SEM microstructure exhibits bigger voids created by the burning away of the carbon particles (pore former). As the pores are very big they are not expected to be eliminated by repeated sintering at 1400 °C, exhibiting the stability of the porous structure which is a prerequisite for the formation of a dense coating of YSZ by the various techniques (e.g. EVD, EPD, and dip coating). It involves repeated heat treatment of the coated tubes at a temperature around 1400 °C, as YSZ and LSM are reported to undergo reactivity around 1400 °C [1]. As the maximum and safe sintering temperature for the YSZ coating on LSM has to be restricted to temperature less than 1400 °C, the tubes formed in this work can act as a potential electrolyte support for formation of SOFCs.

4. Conclusions

The zeta-potential study has shown that the optimum pH for the co-dispersion of both LSM and carbon precursor is 10–11. Studies on rheological behavior of slips exhibited pseudo-plastic flow behavior. Pseudo-plasticity reduced (i.e., reduction in viscosity and yield stress) with decreasing solid concentration, indicating improvement in dispersion. A slip with a solid content of 50 wt.% at a pH of 11 was found to exhibit enough viscosity to suppress segregation (leading to homogeneous microstructure). Still this solid concentration was low enough to exercise easy control over formation of desired thickness. The porosity (35% open porosity) of the sintered bodies was found to remain constant upon further sintering at 1400 °C as the pores were very coarse.

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