

Lanthanum ferromanganites thin films by sol–gel process.

Influence of the organic/inorganic R ratio on the microstructural properties

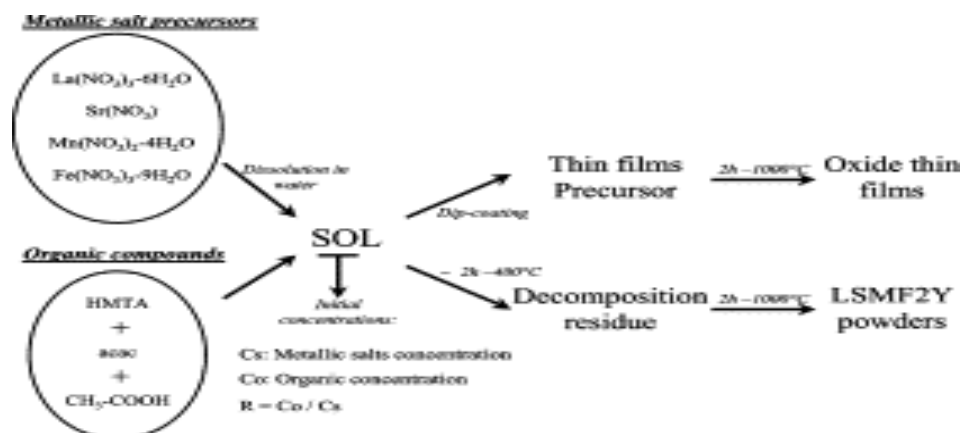
Pascal Lenormand, Simone Castillo, José-Ramon Gonzalez, Christel Laberty-Robert and Florence Ansart

Centre inter-universitaire de recherche et d'ingénierie sur les matériaux, UMR 5085,
université Paul Sabatier, bât. 2R1, 118, route de Narbonne, 31062 Toulouse cedex 4, France

Abstract

Strontium-substituted lanthanum ferromanganites, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3+\delta}$ ($y=0, 0.2, 0.5, 0.8, 1$), LSMF2Y ($Y=10y$) for solid oxide fuel cell (SOFC) cathode applications have been synthesized by a polymeric sol–gel route and deposited on YSZ substrates by a dip-coating process. The influence of the sol synthesis parameters (metal composition, organic and metal salt concentrations) on the thin film microstructure has been investigated. In this study, it has been shown that the organic/inorganic ratio, called R , appears as a key parameter to control the microstructural properties of final coatings.

Graphical abstract



Keywords: Lanthanum ferromanganite oxide; LSMF perovskite; Sol–gel; Thin films

- 1. Introduction
- 2. Experimental
 - 2.1. Material preparation
 - 2.2. Characterization
- 3. Results
 - 3.1. Sol viscosity
 - 3.2. X-ray diffraction of powders
 - 3.3. Thin films microstructural investigations
- 4. Conclusion
- References

1. Introduction

2.

Mixed oxides, particularly those with perovskite structure, have received much attention as cathode materials for solid oxide fuel cells (SOFCs) [1] and [2]. Strontium-substituted lanthanum manganites (LSM) are the usual cathode materials, owing to their chemical stability versus yttria stabilized zirconia (YSZ), which is the conventional electrolyte for SOFC systems [3].

To improve the cathode material conductivity, it is necessary to optimize both composition and microstructure of the electrode. For the oxide composition, the manganese is partially or totally substituted by iron in LSM, in order to obtain both electronic and ionic conductivity [4]. Simultaneously, the microstructure of the synthesized material is controlled by use of a sol–gel method derived from the Pechini process [5]. Thin films of these cathode materials are deposited on a YSZ substrate by a dip-coating process [6]. The dip-coating solution is composed of metal salt precursors dispersed in a polymerizable organic matrix [7] and [8].

In this work, we present the influence of the sol synthesis parameters (oxide composition, organic compounds and/or metal salt concentration) on the microstructure of the obtained thin films.

2. Experimental

2.1. Material preparation

This paper reports on the synthesis of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3\pm\delta}$ ($y=0, 0.2, 0.5, 0.8, 1$) LSMF2Y ($Y=10y$) thin films and the characterization of their microstructural properties. According to Kindermann et al. [9], the substitution ratio of lanthanum by strontium was kept to 20%, optimized value to limit the reactivity between the two active materials (cathode and electrolyte). The manganese was partially or totally substituted by iron.

The dip-coating LSMF2Y solution was prepared according to the polymeric method [7]. Reagent-grade $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%), $\text{Sr}(\text{NO}_3)_2$ (99%), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98%), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%), were used as the starting cation salts. They were precisely weighted at the molar composition of LSMF2Y and then dissolved in distilled water. After the homogenization of this solution, a mixture containing complexing and polymeric agents (hexamethylenetetramine (HMTA), acetylacetone (acac)—in equimolar ratio—and acetic acid (CH_3COOH)) was added to promote polyesterification and polycondensation reactions. The volume of the initial solution was always adjusted to 200 mL by addition of acetic acid.

The metal salt concentration, calculated from the initial solution, was limited by the manganese substitution ratio. According to previous works [10], there was a maximum of metal salt concentration for pH values up to 2 to avoid iron precipitation in the sol. Higher the iron content in the required perovskite, smaller the metal salt concentration of the solution. As the pH is mainly determined by the solvent (acetic acid; $\text{pH} = 3.2$), the cation concentration limit in the sol to obtain a stable solution depends on the iron content. The cation concentrations used in this work were reported in Table 1.

Table 1.

Limit values of cation concentration in the sol as a function of iron content

	LSM20	LSMF22	LSMF25	LSMF28	LSF210
C_s (mol L^{-1})	0.6	0.6	0.18	0.12	0.08

The variation of the initial metal salt concentration for LSMF2Y oxides leads to define the R ratio as “organic compounds concentration” (C_o) [HMTA + acac] on “metal salt concentration” (C_s). The R ratio may be adjusted by modifying one of the concentrations

(organic compounds or metal salts), the second remaining constant. R values used in this work are summarized in [Table 2](#).

Table 2.

R values versus metallic salt concentration C_s and organic compound concentration C_o

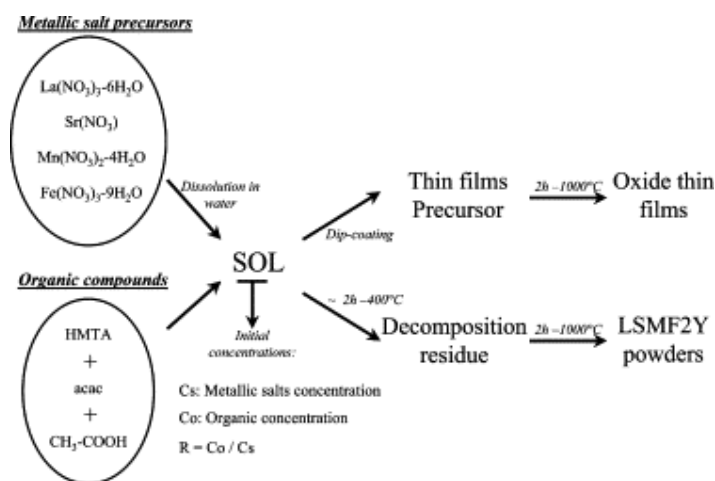
$C_o=1.85 \text{ mol L}^{-1}$					
$C_s \text{ (mol L}^{-1}\text{)}$	0.08	0.12	0.18	0.6	
$R=C_o/C_s$	23.4	15.6	10.4	3.1	
$C_s=0.18 \text{ mol L}^{-1}$					
$C_o \text{ (mol L}^{-1}\text{)}$	1.85	1.44	0.9	0.81	0.56
$R=C_o/C_s$	10.4	8	5	4.5	3.1

After heating at 80–90 °C, the solution became more viscous and the viscosity (measured at 25 °C) was adjusted by controlling the final volume of the sol.

Starting from the sol, both fine powders or thin films were prepared. Powders were obtained by the sol calcination at 400 °C in air followed by heat treatment of the combustion product at 1000 °C in air during 2 h to form the LSMF2Y oxide. Thin films were prepared by dipping yttria stabilized zirconia (YSZ) ceramic substrates in a LSMF2Y polymeric solution of viscosity adjusted to 40 mPa s, and then pulling it up at a constant speed (1 to 5.5 cm min⁻¹). Before coating, YSZ substrates were previously cleaned in an ultrasonic bath successively with acetone and alcohol and dried in an oven at 80 °C. The layers were heat treated up to 1000 °C for 2 h with a heating rate of 100 °C h⁻¹.

Powders and thin films were elaborated for various LSMF2Y compositions and R ratios. The synthesis process is summarized on [Fig. 1](#).

Fig. 1. LSMF2Y powders and thin films synthesis by the polymeric method.



2.2. Characterization

Viscosity measurements of polymeric solutions as a function of R (Co/Cs) were performed with a Tve-05 Lamy viscometer at 25 °C.

X-ray powder diffraction of samples treated at 1000 °C were recorded using Cu-K α radiation source (Siemens D501). The thin layer crystallization was studied using a D5000 diffractometer (Siemens) operating in an asymmetric Debye–Scherrer mode with a grazing incidence angle of 1°.

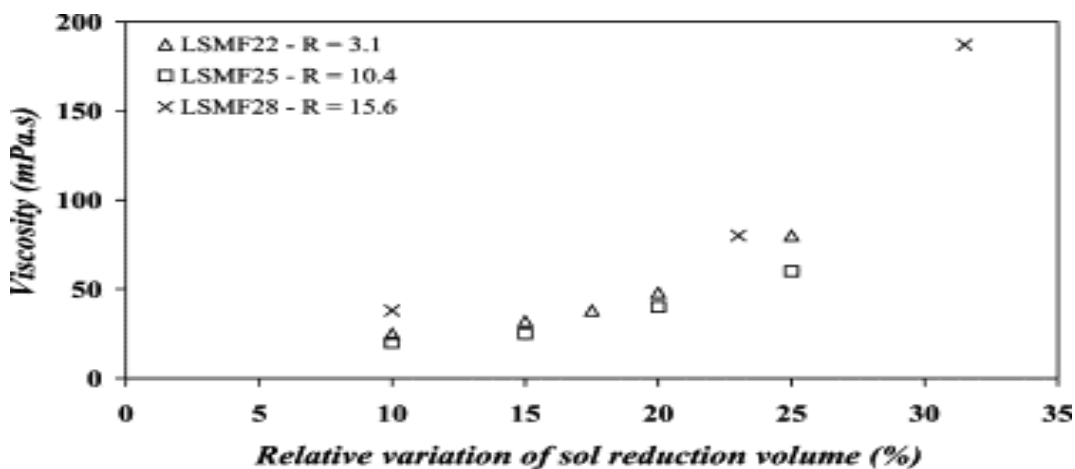
Both surface roughness and thickness of the films were determined by an optical profilometer (Zygometer) operating as a Perrot–Fabry interferometer. The microstructures of LSMF2Y thin films were observed by Scanning Electron Microscope (SEM JEOL; model JSM-35 CF).

3. Results

3.1. Sol viscosity

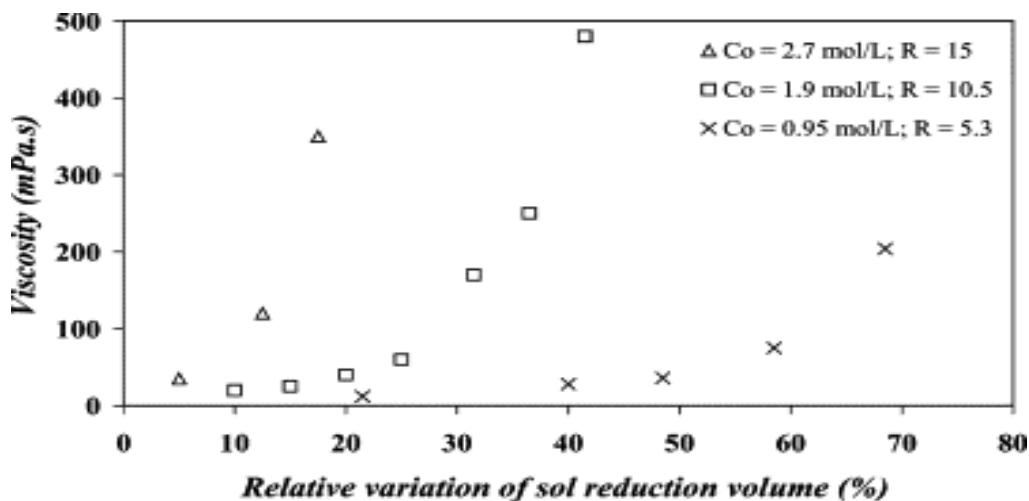
Sol viscosity was measured for various relative variations of reduction volume defined as $[(V_{\text{initial}} - V_{\text{final}})/V_{\text{initial}}] \times 100$. In Fig. 2 was reported the viscosity of the sols LSMF22, LSMF25 and LSMF28 synthesized with a constant organic compound concentration $C_o = 1.85 \text{ mol L}^{-1}$ corresponding to $R = 3.1, 10.4, 15.6$, respectively. The initial metal salt concentration was kept at the previously determined limit value. Whatever the chemical composition and the metal salt concentration, the sol viscosity increased in the same way, according to the relative variation of reduction volume.

Fig. 2. Viscosity of the sol versus reduction volume ($C_o=C_{ste}=1.85 \text{ mol L}^{-1}$).



In Fig. 3 was reported the viscosity of LSMF25 with fixed metal salt concentration ($C_s=0.18 \text{ mol L}^{-1}$), the R ratio values ($R=5.2, 10.4, 15$) resulting from change in organic compound concentration. The sol viscosity was measured for various relative reduction volume. The viscosity sharply increased according to the organic content of the sol. The final sol rheology was only controlled by the organic compound amount.

Fig. 3. Viscosity of the LSMF25 sol versus reduction volume ($C_s=C_{ste}=0.18 \text{ mol L}^{-1}$).



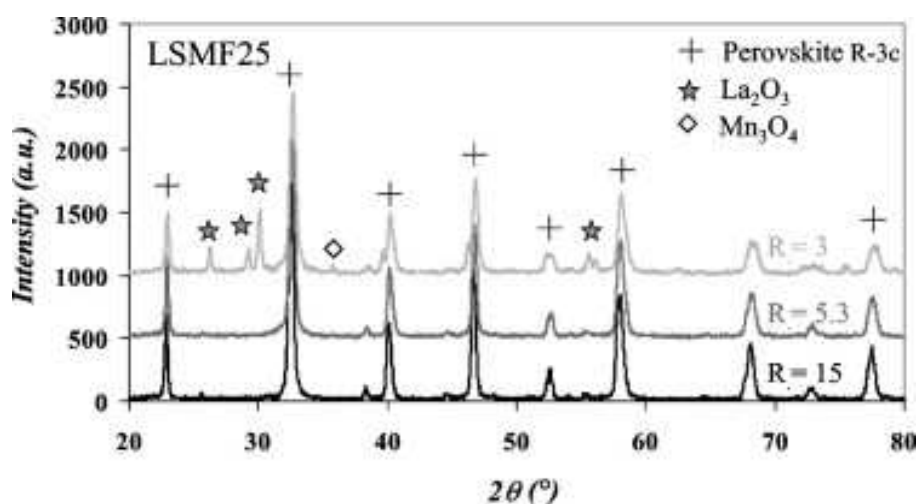
3.2. X-ray diffraction of powders

LSMF2Y powders synthesized from solutions where C_o was kept at a constant value (1.85 mol L^{-1}) and C_s at the previously defined limit value (corresponding to $R=3.1, 10.4, 15.6$ and 23.4) after two hours heating at 1000°C were investigated by XRD. For each composition,

the pure perovskite phase was obtained [10]. Furthermore, LSMF2Y powder chemical content were controlled by Inductively Coupled Plasma (ICP) and were in good agreement with the starting composition of the sol [10].

In Fig. 4, LSMF25 X-ray powder diffraction patterns were presented for various R values ($C_s=0.18 \text{ mol L}^{-1}$). The perovskite phase was always obtained but with $R=3$, the simple oxides La_2O_3 and Mn_3O_4 were also present. As it was previously observed by Gaudon et al., the pure LSM20 mixed oxide ($C_s=0.6 \text{ mol L}^{-1}$) was only obtained for R up to 3.1 [3]. Whatever the metal salt concentration C_s and the mixed oxide composition, a minimal R value (3.1) was required to obtain the pure perovskite phase. This R value seemed to be an intrinsic parameter in this synthesis process; so, it was necessary to introduce a minimal quantity of organic phase to promote a good dispersion of the metal cations in the polymeric matrix.

Fig. 4. XRD patterns of LSMF25 powders heat treated at 1000°C –2 h for various R values ($C_s=C_{\text{ste}}=0.18 \text{ mol L}^{-1}$).



3.3. Thin films microstructural investigations

Microstructures of LSM20, LSMF25 and LSF210 thin films were shown in Fig. 5. These thin films were obtained from the sol by dip-coating (withdrawal speed of the substrate = 1.2 cm min^{-1}) and heat treated at 1000°C in air during two hours. Whatever the iron content, these thin films were homogeneous, continuous and crack-free, some defects observed on the surface being due to the YSZ substrate surface. At high magnification, there was no evidence

of a grain size variation according to the metal salt content or the oxide composition. But, a less porous microstructure was observed for higher iron contents or smaller metal concentrations.

Fig. 5. SEM micrographs (2 magnifications) of LSMF2Y coatings on YSZ substrates after annealing at 1000 °C–2 h ($C_o=C_{ste}=1.85 \text{ mol L}^{-1}$, $\eta=40 \text{ mPa s}$).

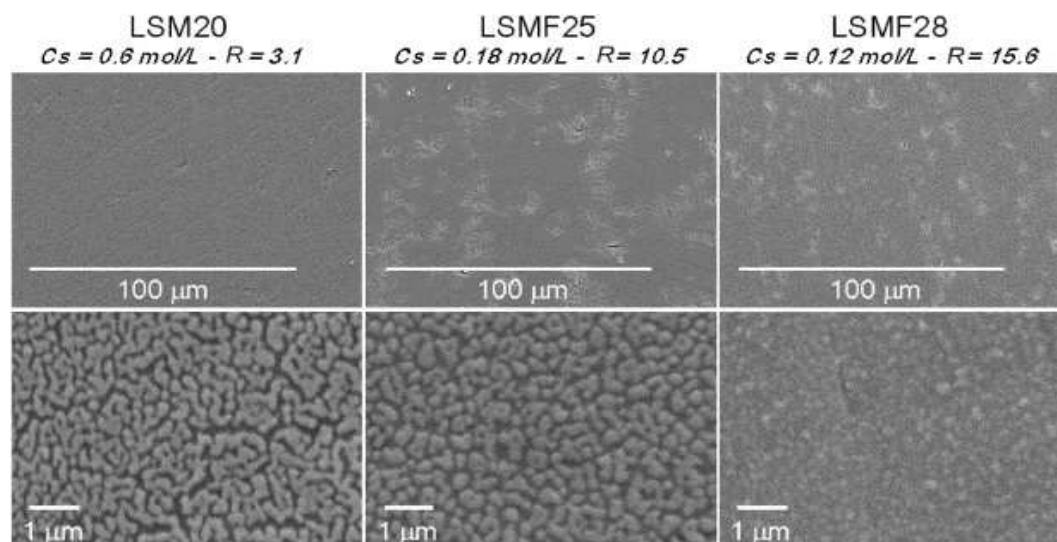
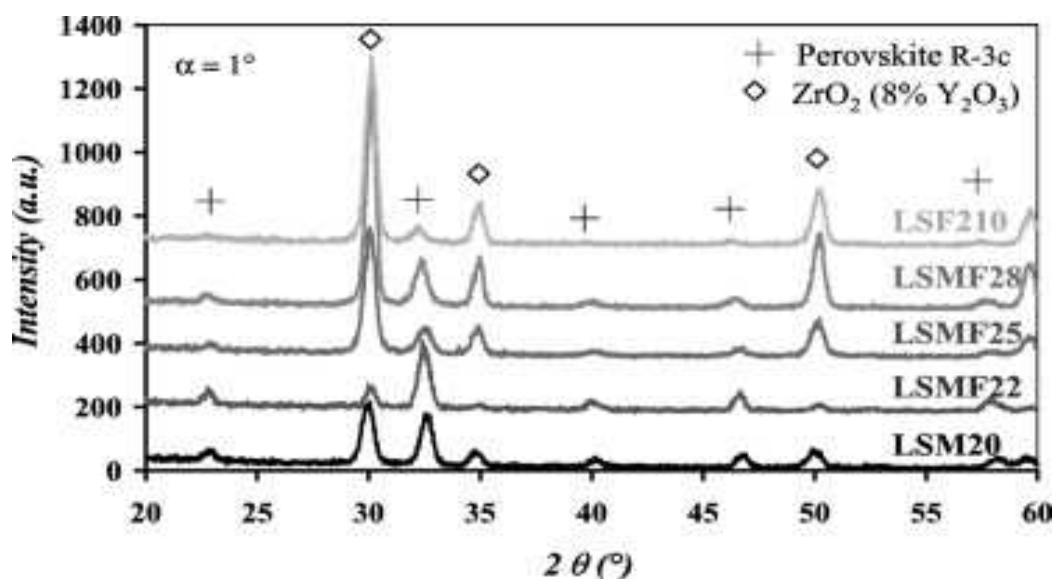


Fig. 6 showed XRD patterns of LSMF2Y thin films deposited on YSZ substrates as a function of iron content. All the peaks were attributed either to the perovskite phase or to the YSZ polycrystalline substrate. Even under a weak incidence angle (1°), the recording of the diffraction peaks of the YSZ substrate was unavoidable, due to the low thickness of the LSMF2Y layer. In addition, the films were polycrystalline with a random orientation. Because of an extensive X-ray diffraction line broadening due to the grazing incidence apparatus, it was not possible to determine precisely the phase symmetries of the films, however, any impurity was detectable.

Fig. 6. XRD patterns of LSMF2Y films heat treated at 1000 °C for various iron content.



The thickness of the thin films measured by optical profilometry were reported in [Table 3](#). The layer thickness decreased as a function of the metal concentration.

Table 3.

LSMF2Y layer thickness versus R values (C_o constant = 1.85 mol L^{-1})

LSMF2Y	LSMF20	LSMF22	LSMF25	LSMF28					
$C_s (\text{mol L}^{-1})$	0.5	0.6	0.18	0.12	LSMF20	LSMF22	LSMF25	LSMF28	LSF210
$R = C_o/C_s$	3.1	3.1	10.5	15.6					
Thickness (nm)	$240 \pm 10^*$	$230 \pm 10^*$	$70 \pm 10^*$	$45 \pm 10^*$					
LSMF2Y									
$C_s (\text{mol L}^{-1})$					0.6	0.6	0.18	0.12	0.08
$R = C_o/C_s$					3.1	3.1	10.5	15.6	23.4
Thickness (nm)					240 ± 10 *	230 ± 10 *	70 ± 10 *	45 ± 10 *	30 ± 10 *

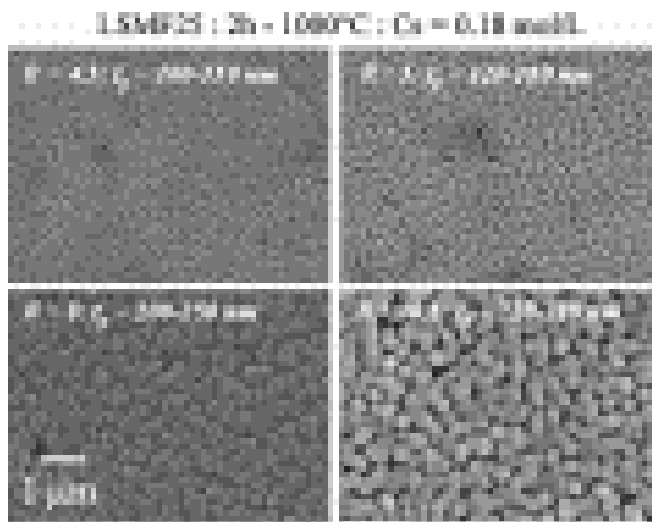
* This accuracy corresponds to the intrinsic roughness of the substrate after polishment.

For an application as SOFC cathodes, the layer thickness must be optimized to 500 nm approximately. To reach the optimal thickness with a low metal salt concentration it would be necessary to deposit several layers.

An other parameter (withdrawal speed) may be increased to raise the initial thickness of the layer (i.e. before heat treatment). The amount of organic compounds to remove is then so

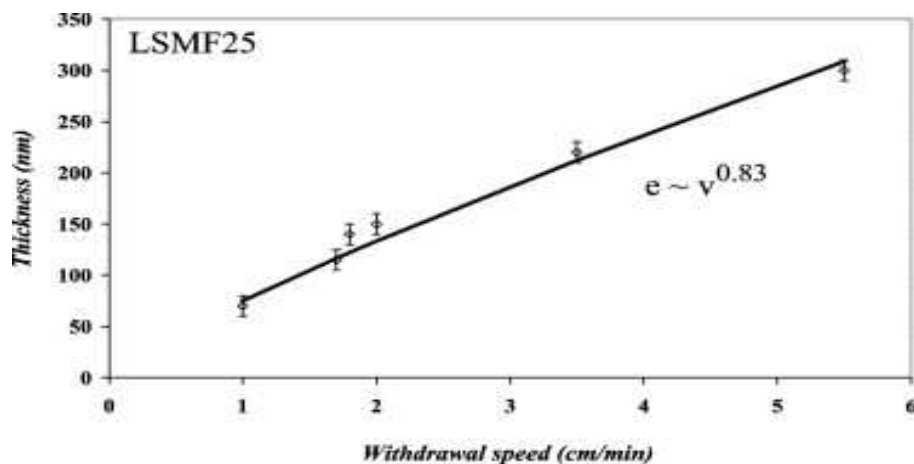
important that a severe cracking of the layer appeared during the thermal treatment step. For a fixed C_s , the ratio R must be reduced to its minimal value i.e. $R=3.1$.

Fig. 9. SEM micrographs of LSMF25 coatings on YSZ substrates after annealing at 1000 °C–2 h ($C_s=C_{ste}=0.18 \text{ mol L}^{-1}$, $\eta=40 \text{ mPa s}$).



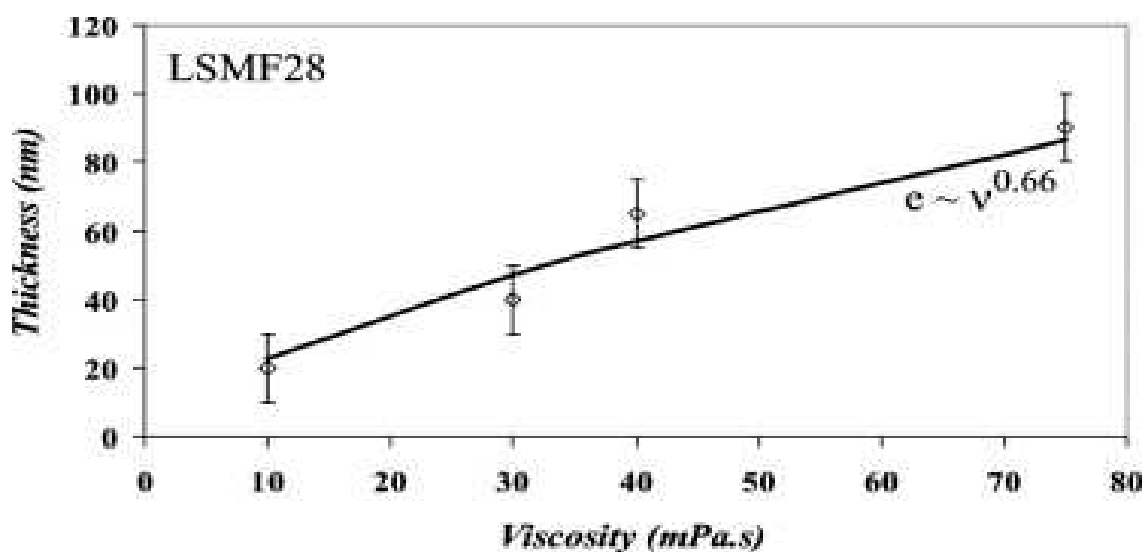
For LSMF25 ($C_s=0.18 \text{ mol L}^{-1}$; $R=3.1$), the layer thickness was reported as a function of withdrawal speed (Fig. 7); it increased as a power function according to the Landau and Levich law, with an exponent value of about 0.83 [11]. Until 3.5 cm min^{-1} , the layers obtained after heat treatment were continuous, homogeneous and crack-free. For this withdrawal speed the thickness was about 220 nm, i.e. of a similar value than those obtained with $C_s=0.6 \text{ mol L}^{-1}$. The metal concentration lowering has been balanced by the increasing of the withdrawal speed, the R ratio being optimized to preserve the quality of the final layer.

Fig. 7. Layers thickness versus withdrawal speed for LSMF25 after annealing at 1000 °C–2 h
($C_s=C_{ste}=0.18 \text{ mol L}^{-1}$; $R=3.1$).



LSMF25 layer microstructure was investigated as a function of R ratio with C_s constant ($C_s=0.18 \text{ mol L}^{-1}$). The SEM micrographies (Fig. 8) for R varying from 4.5 to 10.5 shown an homogeneous distribution of the particle size which increased from 120 to 250 nm approximately.

Fig. 8. Layers thickness versus viscosity of the sol for LSMF28 after annealing at 1000 °C–2 h ($C_s=C_{ste}=0.12 \text{ mol L}^{-1}$; $R=8$).



4. Conclusion

The strontium substituted lanthanum ferromanganites (LSMF2Y) have been synthesized by a polymeric sol–gel route and deposited on YSZ substrates by a dip-coating process. The R ratio, defined as organic phase concentration on metallic phase concentration, is the main sol parameter governing both the purity of the obtained phases and the microstructure of the films. The amount of organic compounds must ensure an homogeneous dispersion of the metal cations in the polymeric matrix. As a function of the metallic salt concentration, the R ratio always must be upper than 3.1.

The rheology of the polymeric sol is only related to the organic compound amount and must be controlled to obtain continuous, homogeneous and crack-free thin films. For iron rich compounds, a minimal R ratio allows to deposit an equivalent quantity of matter by increasing the withdrawal speed. In this case, crack-free films of optimized thickness are prepared.

References

- M.Q. Nguyen, *J. Amer. Ceram. Soc.* 76 (1993) (3), p. 563.
- J.A.M. Van Roosmalen, J.P.P. Huijsmans and L. Plomb, *Solid State Ionics* 66 (1993), p. 279.
- M. Gaudon, Ph.D. Thesis, University Paul Sabatier, Toulouse, France, 2002.
- G. Caboche, L.-C. Dufour and F. Morin, *Solid State Ionics* 144 (2001), p. 211.
- P. Pechini, Patent 3,330,697 (July 11, 1967).
- C.J. Brinker and G.W. Scherrer, *Sol–Gel Science*, Academic Press (1990).
- I. Maurin, P. Barboux and J.P. Boilot, *Mater. Res. Soc. Sympos. Proc.* (1997), p. 453.
- M. Gaudon, C. Laberty-Robert, F. Ansart, P. Stevens and A. Rousset, *Solid State Sci.* 4 (2002), p. 125.
- L. Kindermann, D. Das, D. Bahadur, R. Weiss, H. Nickel and K. Hilpert, *J. Amer. Ceram. Soc.* 80 (1997), p. 909.

P. Lenormand, C. Laberty-Robert and F. Ansart, *France–Deutschland Fuel Cell Conference Proceedings* (2002), p. 248.

L.D. Landau and B.G. Levich, *Acta Physiochem. URSS* 17 (1942), p. 112.

Original text on Elsevier.com