

## A CO-PRECIPIATION PROCEDURE FOR THE SYNTHESIS OF LSM MATERIAL

### SOOBARJANJE LSM ZA PRIPRAVO KATODNIH MATERIALOV ZA GORIVNE CELICE

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Lanthanum manganite substituted with strontium is a strong candidate for use as a mixed conductor at the cathode site in solid-oxide fuel-cell systems. In the present work a co-precipitation method for the preparation of LSM is described and some material properties are reported. Since the co-precipitation involved calcination at 1000 °C and subsequent sintering, the crystalline phase development and the material homogeneity were followed by X-ray powder diffraction. It was found that no secondary crystalline phases were present in the system when the samples were thermally treated up to 1200 °C. The sintering behaviour of the calcined powders and their density evolution are also reported. Relatively dense bodies were prepared after thermal treatment at 1200 °C for 2 hours. The electrical characteristics of the material were determined from screen-printed LSM sintered layers. The electrical conductivity of the screen-printed layers increased with the sintering temperature due to an additional densification effect. Porous LSM bodies were prepared by methyl cellulose admixing as a pore-former.

**Key words:** co-precipitation, lanthanum strontium manganite, microstructure, electrical conductivity

Najpogosteje uporabljan katodni material v visokotemperaturni izvedbi gorivnih celic (SOFC) je lantanov manganit, dopiran s stroncijem (LSM). LSM s sestavo  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_{3-\delta}$  smo pripravili z novo metodo soobarjanja iz raztopine karbonatov. Oborino smo po filtraciji in spiranju sušili pri 110 °C in nato kalcinirali pri 1000 °C. Po kalcinaciji pri različnih temperaturah in po sintranju smo prahove analizirali z rentgensko praškovno analizo. Materiali so po sintranju vsebovali le perovskitno kristalno obliko lantanovega manganita. Parametre sintranja prahov LSM po kalcinaciji pri 1000 °C smo določili s segrevalnim mikroskopom. Vzorce LSM z dodatkom tvorca por in brez njega smo po sintranju analizirali z elektronsko mikroskopijo. Električne karakteristike tiskanih plasti LSM smo določili s štiritočkovno metodo. Specifična električna prevodnost pripravljenih plasti LSM je primerljiva z literaturnimi podatki za materiale LSM, ki so bili pripravljene po kalcinacijskem postopku.

**Gljučne besede:** koprecipitacija, lantanov stroncijev manganit, katoda, mikrostruktura, električna prevodnost

## 1 INTRODUCTION

Lanthanum strontium manganite (LSM) is known as a potential cathode material for solid-oxide fuel cells (SOFCs) based on a stabilized zirconia electrolyte<sup>1</sup>. In the present generation of SOFCs a nominal composition of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $x < 0.2$ ) is normally used. The use of LSM-based cathode materials depends not only on their chemical, structural and thermodynamic characteristics but also on their final microstructure, grain size, pore size and pore-size distribution<sup>2-4</sup>. The porosity and pore-size distribution, in particular, play a significant role because of the double role of the LSM in the SOFC system, i.e., the LSM has to be an effective electro-catalyst and at the same time has to be permeable to cathode gases.

Another aspect when LSM is used as the cathode material is its homogeneity and the possible interaction with the zirconia-based electrolyte. One potential interaction between the LSM cathode layer and the zirconia-based electrolyte in the SOFC system is diffusion (at the phase boundary) of the  $\text{Y}_2\text{O}_3$  from the YSZ into the LSM phase. This diffusion leads to the formation of tetragonal and/or monoclinic  $\text{ZrO}_2$ . Such a  $\text{ZrO}_2$  crystal-structure transformation is accompanied by

a volume change and, as a result, possible crack formation (more intense when the SOFC system is repeatedly heated up and cooled down)<sup>5</sup>. Another problem arises if products with a high electrical resistivity at the cathode/electrolyte phase boundary, like  $\text{La}_2\text{Zr}_2\text{O}_7$ , are formed. The  $\text{La}_2\text{Zr}_2\text{O}_7$  phase is normally found in systems based on  $\text{LaMnO}_{3+d}/\text{YSZ}$  after a prolonged treatment at high temperatures<sup>6</sup>. To suppress the  $\text{La}_2\text{Zr}_2\text{O}_7$  formation, La-manganite is doped with Sr in relatively low concentrations

( $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ;  $x < 0.3$ ). Larger additions of Sr also mean a higher risk of new low-conducting  $\text{SrZrO}_3$  phase formation. The reactions between LSM and YSZ are more pronounced at higher temperatures, lower oxygen partial pressures and for prolonged reaction times.

The microstructure and homogeneity characteristics of LSM depend to a large extent on the processing conditions and are hard to control in the conventional ceramic synthesis process, which is based on the diffusion of the components in the solid state at high temperatures. For this reason alternative preparation routes for LSM synthesis based on wet chemical methods have been proposed. A characterization of perovskite powders for the cathode and oxygen

membranes prepared by different chemical routes was made by Sefir et al. <sup>7</sup>, while the effect of the synthesis route on the catalytic activity of LSM was studied by Bell et al. <sup>8</sup>. The results of these studies implied that the carbonate co-precipitation synthesis route delivers a finer powder with more homogeneous composition and surface structure and is thus more suited for mixed conductor applications in SOFC systems. They both based the LSM preparation on the carbonate co-precipitation method, following the route described by Tanaka et al., where  $\text{Na}_2\text{CO}_3$  was used as the precipitating agent <sup>9</sup>. Another co-precipitation-based LSM preparation was developed by Ghosh et al. <sup>10</sup> using ammonium carbonate as the precipitating agent.

In the present work we applied the carbonate co-precipitation route for batch LSM preparation. Sintering and microstructure-development studies were carried out for the calcined powder. Prepared LSM bodies were also characterised in terms of their electrical conductivity. Since a requirement of the cathodes for a SOFC is a porous body with almost 40 % open porosity, we also modified the cathode material by the addition of a former.

## 2 EXPERIMENTAL

In order to prepare stock solutions of 0.5-M lanthanum nitrate and strontium nitrate, lanthanum oxide ( $\text{La}_2\text{O}_3$ ) and strontium carbonate ( $\text{SrCO}_3$ ) were separately carefully dissolved in concentrated nitric acid, while manganous nitrate ( $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) was dissolved in distilled water. Predetermined amounts of each solution were then mixed for  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$  preparation. The mixed solution was added drop-wise to a precipitating bath containing an aqueous solution of ammonium carbonate in which the amount of ammonium carbonate was in 50 % excess for complete precipitation of the mixed La-Mn-Sr-precursor. The pH of the precipitating bath was kept constant at 8.0 by small additions of aqueous ammonia. The temperature of the reaction mixture in the precipitating bath was adjusted to 65 °C and kept constant. The precipitation reaction took place in a  $\text{CO}_2$  atmosphere to prevent any undesired oxidation of the manganese to  $\text{MnO}_2$ . The reaction time for the complete co-precipitation process was approximately 3 h.

The precipitate was easily filterable, and after filtration was washed several times with 0.125-M aqueous ammonium-carbonate solution. The washed precipitate was dried, first at room temperature under a  $\text{CO}_2$  atmosphere for several hours, and afterwards, for 6 hours at 110 °C in air. Prior to calcination in a muffle furnace at 1000 °C for 1 hour, the dried powder was ground in an agate mortar. Calcined LSM powders were wet milled in isopropanol, pressed into tablets ( $\Phi = 6$  mm,  $h = 4$  mm,  $p = 70$  MPa) and sintered at (1150, 1200 and 1250) °C for 1 h.

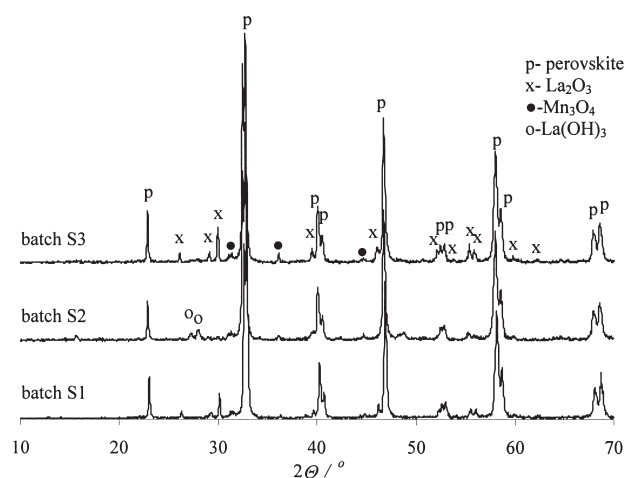
The carbonate co-precipitation route described above is also suitable for the preparation of larger quantities of mixed La-Sr-Mn-carbonate. The method is also very reliable and the final precipitate is easy to reproduce. To corroborate the above statement we prepared mixed La-SrMn carbonate in three different batches (S1, S2, and S3) and compared some of their properties. Typical quantities of initial precursors consumed in one cycle of the bath precipitation were 100 g of  $(\text{NH}_4)_2\text{CO}_3$  dissolved in 2.5 L of  $\text{H}_2\text{O}$ , 854 mL of 0.5-M Mn-precursor solution, 363 mL of 0.5-M La precursor solution, and 128 mL of 0.5-M Sr precursor solution. Such a reaction mixture yielded approximately 100 g of final calcined LSM powder. Samples were characterized with the X-ray powder-diffraction technique using D4 ENDEAVOR apparatus. The shrinkage during sintering was measured by a LEITZ WETZLAR heating microscope.

LSM samples with the mass fraction of 10 % of pore former (methyl cellulose) were mixed in a ball mill for (3, 30 and 180) min, pressed into pellets and then sintered at 1200 °C for 1 h. After sintering the samples were polished and thermally etched and analyzed with an SEM (Zeiss FE SUPRA 35 VP). The quantitative analyses of the microstructures was performed using a Zeiss KS300 3.0 image-analysis system.

Samples for the electrical measurements were prepared by screen-printing LSM pastes on alumina substrates. Prior to printing the LSM powder was dispersed in an organic liquid phase in ratios from 40 % solid LSM powder and 60 % liquid phase, and then submitted to a homogenization procedure.

## 3 RESULTS AND DISCUSSION

The calcined powders (for XRD study purposes the calcination of the precursor carbonate-hydroxide powder was carried out in the temperature range 1000–1300 °C)



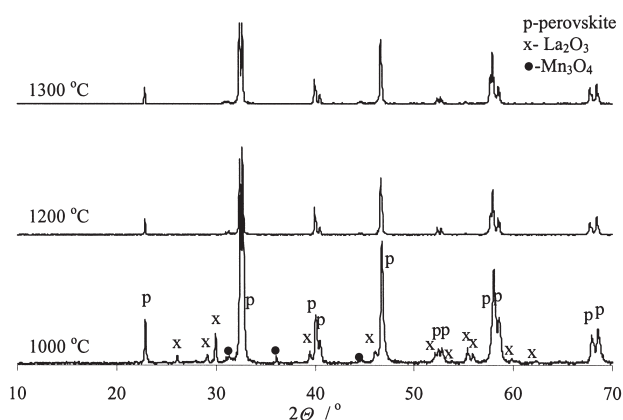
**Figure 1:** XRD patterns of the powder samples calcined at 1000 °C  
**Slika 1:** Praškovni posnetki vzorcev, kalciniranih pri 1000 °C

were submitted to XRD examination. The XRD patterns of the powder samples prepared from the three different batch experiments calcined at 1000 °C are shown in **Figure 1**.

According to **Figure 1** perovskite LSM phase formation (LSM XRD peaks are denoted with the letter p) is practically complete; after calcination at 1000 °C the LSM perovskite phase is quite well crystallised. XRD analysis revealed only traces of the residual secondary phases  $\text{Mn}_3\text{O}_4$  and  $\text{La}_2\text{O}_3$  or  $\text{La}(\text{OH})_3$  resulting from the reaction of lanthanum oxide with moisture, forming lanthanum hydroxide (all denoted in **Figure 1**). The relatively small amount of secondary phases in the sample calcined up to 1000 °C makes the co-precipitation method favourable when compared to synthesis processes that are based on the diffusion of the components in the solid state (in this case the amount of secondary phases is normally greater). If the calcination temperature is increased (1200 °C or 1300 °C, **Figure 2**) the secondary phases are completely dissolved in the perovskite structure.

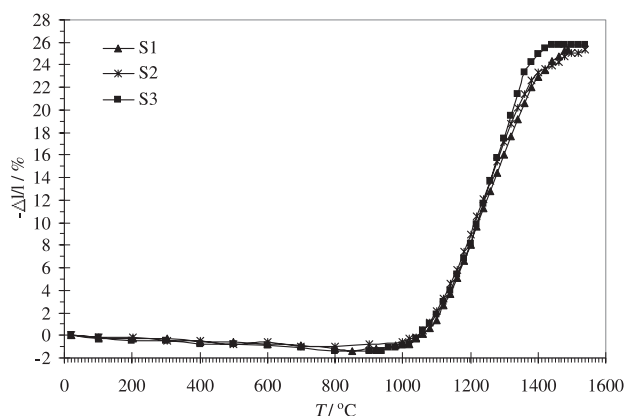
The shrinkage behaviour of the LSM powders prepared with other batch experiments and calcined at 1000 °C are shown in **Figure 3**. All the samples exhibit a normal thermal expansion in the temperature range below 1000 °C. This region of thermal expansion is followed by a single region of rapid sintering. The rate of rapid shrinkage varies slightly for each sample, which may be a consequence of some differences during the wet milling process. Above 1300 °C the powder shrinkage curves show a flattened region, this is due to completion of the rapid sintering stage and the initiation of the final sintering stage with closing of the entrapped porosity. The final shrinkage ( $25.8 \pm 0.4$  %) of different LSM batches does not diverge substantially.

The shrinkage behaviour of LSM powders prepared with other batch experiments and calcined at 1000 °C are shown in **Figure 3**. All samples exhibit normal thermal



**Figure 2:** XRD patterns of the powder S1 calcined at different temperatures

**Slika 2:** Praškovni posnetki vzorca S1, kalciniranega pri različnih temperaturah



**Figure 3:** Typical shrinkage curves of LSM powders prepared in different batch experiments

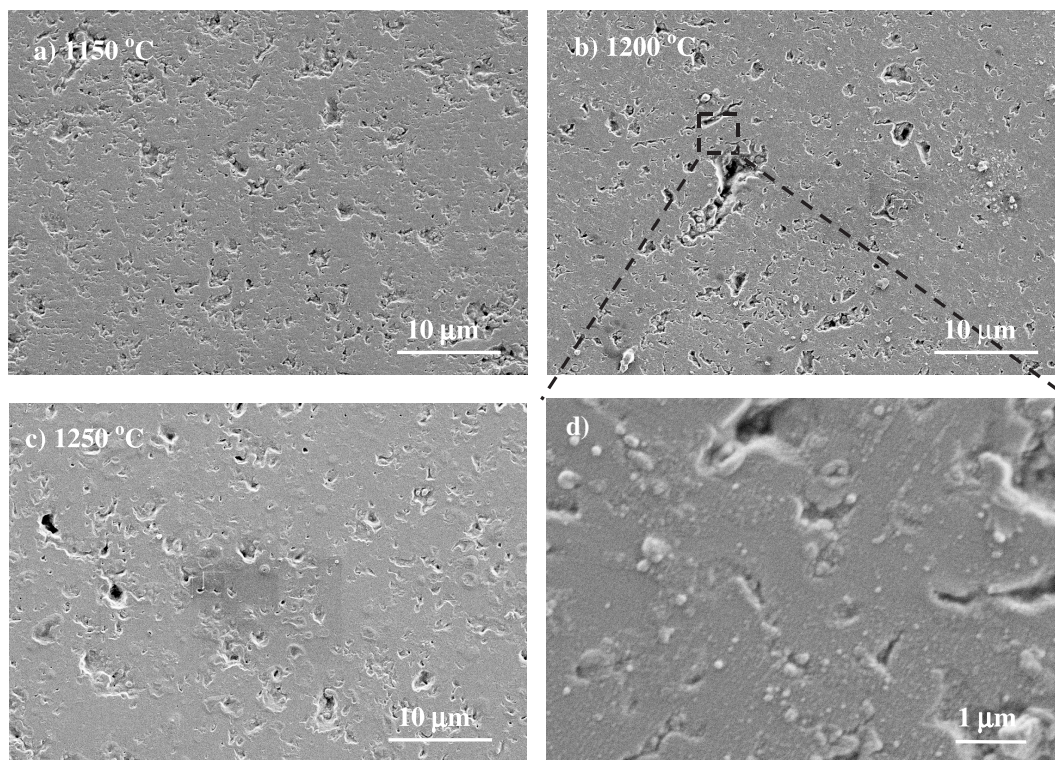
**Slika 3:** Značilne krivulje sintranja vzorcev LSM za tri poskuse obarjanja

expansion in the temperature range below 1000 °C. This region of thermal expansion is followed by a single region of rapid sintering. The rate of rapid shrinkage varies slightly for each sample, which may be a consequence of some differences during the wet milling process. Above 1300 °C the powder shrinkage curves show a flattened region, this is due to completion of the rapid sintering stage and initiation of the final sintering stage with closing of the entrapped porosity. The final shrinkage ( $25.8 \pm 0.4$  %) of different LSM batches does not diverge substantially.

Considering the results of the sintering curves, the sintering temperatures and sintered densities were calculated for all batch-prepared LSM materials. The sintering started at approximately 1050 °C. The sintering temperature and the sintered density varied from 1250 °C to 1280 °C with an average value calculated to be 1265 °C, and 5.61 g/cm<sup>3</sup> to 6.10 g/cm<sup>3</sup>, with an average calculated value 5.84 g/cm<sup>3</sup>, respectively. The shrinkage process finished at approximately at 1390 °C.

Scanning electron micrographs of an average LSM sample (batch S3) sintered at different sintering temperatures (1 hour of sintering) are presented in **Figure 4**. In general, with increasing sintering temperature the LSM microstructure becomes denser. However, the three microstructures presented (**Figure 4a–d**) do not differ significantly, implying that LSM can be successfully sintered, even at 1150 °C.

The above micrographs show a microstructure with denser regions as well as regions with some porosity in the micrometre range. If the dense regions are examined in greater detail (**Figure 5**), excellent particle-to-particle packing can be seen. These regions contain practically no porosity. Such a microstructure with completely dense regions separated by micrometer-range pores could be a consequence of insufficient powder homogenization prior to the sintering tests. Namely, any larger agglomerates left in the powder material after the wet-milling process would cause differences in the



**Figure 4 (a–d):** SEM micrograph of LSM material sintered at different temperatures  
**Slika 4 (a–d):** Posnetki vzorcev LSM po sintranju pri različnih temperaturah

density through the sample. However, the fact that the LSM powder can be sintered at relatively low temperatures (less than 1200 °C, if the material is properly treated prior to sintering) is very important from the applicability point of view. If the material is used as a cathode in SOFC systems then sintering temperatures above 1200 °C may cause some highly undesirable reactions with neighbouring materials.

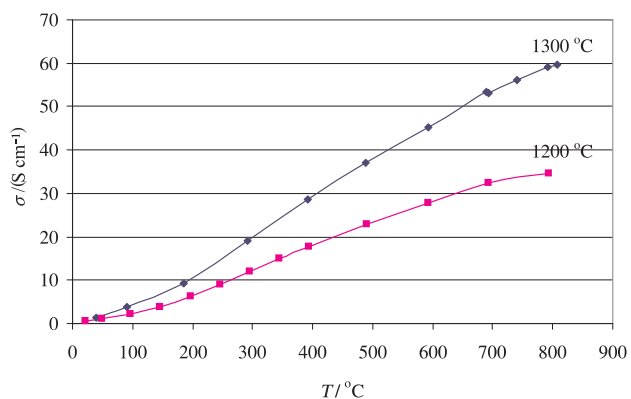
The specific conductivities of screen-printed LSM layers on Al<sub>2</sub>O<sub>3</sub> substrates, sintered at 1200 °C and 1300 °C, are shown in **Figure 6**. The electrical conductivity

was measured by the four-probe technique. The electrical conductivity of the sample sintered at 1300 °C and measured at 800 °C was found to be 60 S/cm, and for the sample sintered at 1200 °C, 35 S/cm. As expected, the results show that a higher sintering temperature increased the material's electrical conductivity. According to the literature, in samples sintered at 1400 °C the electrical conductivity is increased to 65 S/cm, exclusively due to the additional effect of densification (10). The relatively high measured specific electrical conductivity at 1300 °C (and even at 1200 °C)



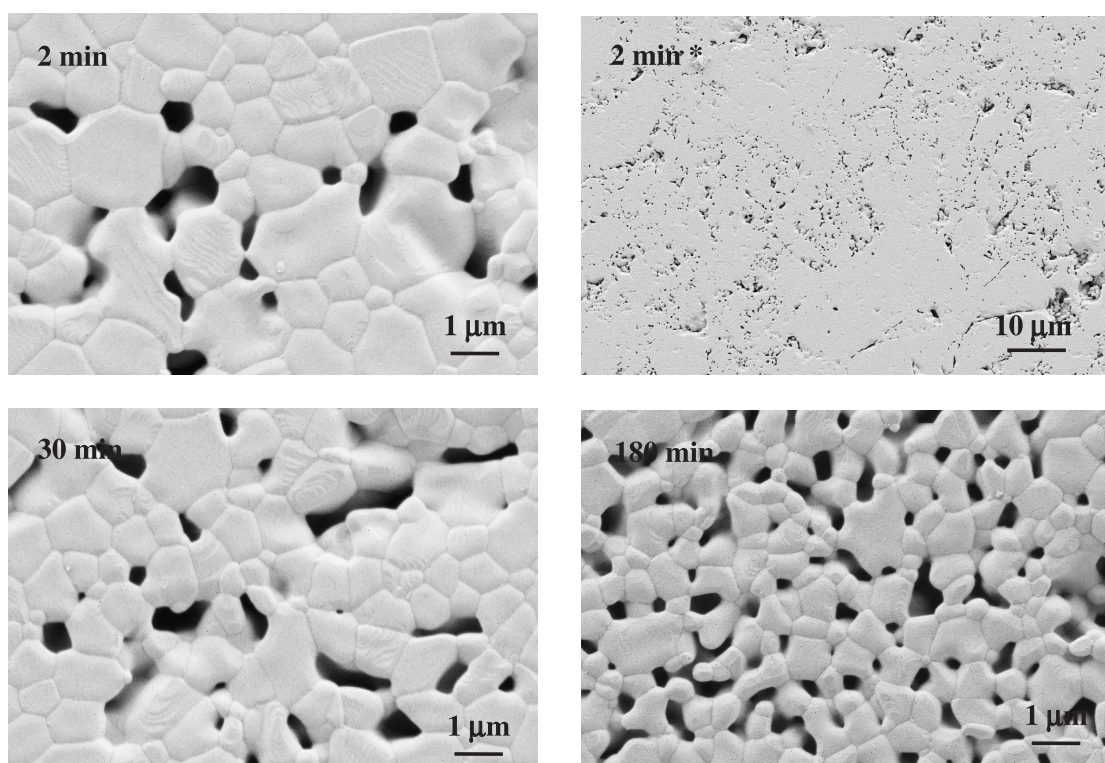
**Figure 5:** Microstructure of polished and thermally etched sample S1 after sintering at 1150 °C (the dense region)

**Slika 5:** Mikrostruktura vzorca S1 po sintranju (1150 °C), poliranju in termičnem jedkanju (gosto področje)



**Figure 6:** Measurements of specific electrical conductivity for samples sintered at 1200 °C and 1300 °C

**Slika 6:** Specifična električna prevodnost vzorcev, sintranih pri 1200 °C in 1300 °C



**Figure 7:** SEM micrographs of LSM material with the addition of the mass fraction 10 % pore former for different times of homogenization in the ball mill

**Slika 7:** SEM-posnetek materiala LSM z 10-odstotnim dodatkom por, ki so nastale pri različnih časih homogenizacije pri mletju

also means that good particle-to-particle contact had already been established at these temperatures.

Some special applications of LSM-based materials require not only excellent contact between the particles but also a relatively high open porosity. To test the ability to form such porous LSM bodies with good particle-to-particle contact, methyl cellulose as a pore-former was admixed prior to tablet shaping and sintering.

After methyl cellulose addition an increase in the porosity after different mixing times in the ball mill was observed for the sintered LSM samples containing mass fraction 10 % of pore former. The scanning electron micrographs in **Figure 7** show that for a mixing time of 2 minutes the sample is composed of dense and less-dense regions. Less-dense regions contain larger several-micrometre-sized pores, while the more-dense regions contain smaller micron or sub-micrometre pores. This relatively high inhomogeneity in the material microstructure is a consequence of an insufficient homogenization time. Using image-analysis software (Karl Zeiss KS 300 3.0) the porosity in the dense regions was estimated as 5.8 %, while the overall porosity (calculated from the material's geometrical density) reached 11.5 %. After 30 minutes of homogenization time the microstructure of the material still revealed differences in density throughout the sample, yielding 7 % porosity in dense regions and 23.9 % overall porosity.

A superb microstructure was achieved after 180 min of homogenization, with no substantial differences in the material's microstructure throughout the sample (33.7 % of overall porosity). Considering the fact that the electrical conductivity in the latter case still remains very close to that of the dense sample, such a microstructure could already be applied at the cathode site in a potential SOFC system.

#### 4 CONCLUSIONS

LSM was synthesized by a non-conventional wet-chemical method. This co-precipitation route included mixed La-Sr-Mn carbonate preparation and its subsequent thermal treatment. Calcined LSM powders after treatment at 1000 °C were very crystalline, with only traces of secondary phases, which completely dissolved in the LSM perovskite structure after heating to 1200 °C. The sintering characteristics of the prepared LSM powders revealed that dense structures could be prepared at sintering temperatures as low as 1150 °C, but the problem of powder homogenization prior to sintering has still to be solved. The specific electrical conductivity of sintered LSM elements reached 35 S/cm (measured at 800 °C) after sintering at 1200 °C and 60 S/cm (measured at 800 °C) after sintering at 1300 °C. Such a relatively high electrical conductivity is believed to be a consequence of the good powder sinterability and hence

the excellent particle-to-particle contact. Homogeneous sintered bodies with a higher porosity, but still good contact between the particles, were achieved after admixing methyl cellulose as a pore former and a prolonged homogenization of 180 min in a ball mill, with subsequent sintering at 1200 °C.

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