



CATHODES BASED ON LANTHANUM MANGANESE FOR SOLID OXIDE FUEL CELLS

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abstract: Solid oxide fuel cells (SOFCs) are electrochemical ceramic devices operating at high temperature as power generators for the future with high efficiency and low emissions. The paper presents our studies for synthesis and characterization of electrode ceramic materials for SOFC devices selected for cathodes from the $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ perovskite-type compositions with $\text{M}=\text{Sr}$ and $x=0.55$. The material obtained was characterized by XR diffraction, scanning electron microscopy, measurements of density and porosity. The influence of Sr doping on the phase structure development and on sintering behaviour was investigated. The results were correlated with electrical conductivity data up to 800°C. The role/importance of a stable monophasic perovskite structure for the best electrode performances was confirmed.

key words: ceramic electrodes; cathode; fuel cells; perovskite compounds; electrical conductivity.

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1. Introduction

At present alternatives are sought to obtain electric energy based on technologies offering maximum efficiency, high reliability and lowest environment pollution. In this respect, fuel cells are considered the cleanest technology to obtain sustainable energy.

SOFCs are energy producing facilities based on direct conversion of gaseous fuels (hydrogen, natural gas, coal gas, ethanol, methanol etc.) capable to reduce pollutant emissions of NO_x , SO_x and greenhouse gas CO_2 . In the last period, The SOFC technology has made major progress concerning both power density and life expectancy [1-5].

The materials used to build the cell components (electrolyte, electrodes) play a major role in the domain of the low temperature solid oxide fuel cells.

Besides the electrolyte, SOFC cell performances are also influenced by the electrodes. The electrodes actually represent the support and activators for the electrochemical reactions, insuring also the charge carriers transport, totally for electrons and to some extent for ions [1-5].

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Electrodes form together with the electrolyte a triple phase boundary region gas-electronic solid-ionic solid, where the mechanism of electrical conduction suddenly changes from ionic to electronic.

The use of ceramic materials as electrodes has been the most advantageous solution currently accepted. The eligible oxide compounds show at the working temperature of the cell (800-1000°C) predominantly electronic type electrical conduction. As in the case of the electrolyte materials, the electrical conductivity characteristic is influenced at the lattice structure level by electron hole defects.

Generally, cathode materials are MO, MO₂ and ABO₃ oxides showing a perovskite-type phase structure. The formation of defects takes place through a doping process with cations of different valence, resulting in a valence state transition for the cation being replaced by doping [6-9].

Pursuing researches for new types of electronic conductor oxide compounds at high temperatures has led to the development of perovskite material groups based on Ca, Sr, Zn doped lanthanum chromites and manganites. For these compounds, the partial substitution process of La with Ca or Sr leads to the increase of the electronic defects amount and also results in an increase of the material chemical stability.

The most known compositions developed are of the La_{1-x}Sr_xMnO₃, La_{1-x}Sr_xCrO₃, La_{1-x}Sr_xCoO₃ and La_{1-x}Ca_xCrO₃ type.

The aim of this paper is to investigate the sintering behaviour of the ceramic material in correlation with phase structure and electrical properties of the perovskite type composition La_{0,45}Sr_{0,55}MnO₃ [10-14].

2. Experimental

The preparation method of the La_{0,45}Sr_{0,55}MnO₃ (LSM) cathode composition was built on solid state reactions comprising high purity metal oxides and carbonates from Fluka and Merck.

The raw materials were dosed gravimetrically and wet homogenised for six hours at a ratio dry matter:water:balls of 1:2:2.

After drying of the material at 70°C for 4 hours, the powder was granulated on the 0.8 mm and the 0.41 mm screen, subjected to briquetting and calcinated at 900°C. Aiming at better porosity of the cathode composition, a pore former was used, The mix was wet homogenised with the pore former for 7 hours. From the dried powder discs of Ø17 x 0,5-0,6 mm were uniaxially pressed at 2tf/cm². The test pieces were thermally treated in the electric furnace, at different temperatures - 1100°C and 1150°C – by being maintained for 2 hours at the maximum temperature. Cooling of the samples was conducted freely, together with the furnace cooling.

Characterisation methods

The thermally treated samples were used to determine the apparent density by the immersion method, using a hydrostatic balance AND model GH200, with 0.1% precision. Measurements were conducted on at least three test pieces of ceramic material.

The final composition of the sintered samples was determined by X-ray diffraction on the sintered test specimens, using an X-ray diffractometer *BRUKER AXS D8 Advance* with radiation Cu_α and a K_β filter of Ni.

The texture of the samples was examined with a scanning electron microscope FESEM-FIB type Gemini SEM column with a minimum resolution of 1 nm at 15 kV.

Electrical conductivity was measured by impedance spectrometry. The impedance spectroscopy measurements were made within the temperature domain 850-1200 K. The real and the imaginary part of the complex impedance were acquired in the frequency domain from 100 Hz to 1 MHz, for an amplitude of 100 mV, using the frequency response analyser Solartron SI 1260 with accuracy of 0.1% and 0.1°.

3. Results and discussion

Apparent density and porosity

The results obtained by the characterisation of heat treated samples are shown in Table 1. One observes that at both sintering temperatures the samples have apparent porosity > 20%, values corresponding to cathodic materials for SOFC. This porosity has to be between 20-40 %.

Table 1 Physical properties.

Sample	Sintering temperature (°C)	Water absorption (%)	Apparent density (g/cm ³)	Apparent porosity (%)
LSM	1000	9,30	3,32	30,40
	1150	8,62	3,50	26,72

For the sample LSM a continuous decrease of water absorption depending on the firing temperature was observed, but to a very limited extent.

Mineralogical composition

The X-ray diffraction results (Fig. 1) have put in evidence the accomplishment of the perovskite type phase structure with distorted rhombohedral hexagonal symmetry, typical for a lanthanum manganite compound – LaMnO_3 . The formation of the distorted structure is due to the incorporation of the Sr dopant into the crystal lattice on La sites by cationic substitution.

This behaviour of the LSM composition with totally hexagonal symmetry also shows crystallisation degree and phase stability typical to a perovskite type compound.

Microscopy

Electronic microscopy conducted on the LSM sample fired at 1000°C as well as on that fired at 1150°C (Fig. 2) puts in evidence the formation of a homogenous microstructure comprising individualised component particles of hexagonal shape, typical for the perovskite composition and large pores. For the samples fired at 1000°C, the structure of the material shows small crystallites (<300 nm), surrounded by irregularly distributed pores. With increasing of firing temperature, the growth of crystallites >460 nm and the occurrence of large pores are observed.

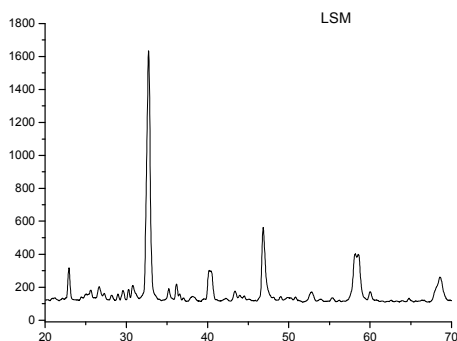


Fig. 1 *Diffractogramm of the perovskite LSM type cathode composition.*

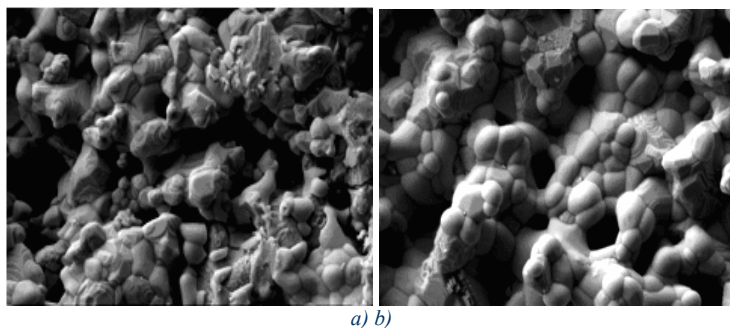


Fig. 2 *SEM Micrographs of the LSM sample treated: a) at 1100°C and b) at 1150°C.*

Electrical conductivity

The shape of the Bode representation, $\ln|Z| = f(\nu)$ and $\theta = f(\nu)$ (not shown) indicated the possibility of description of the electrical behaviour of the sample by the equivalent circuit shown on the right in Fig. 3, comprising an electrical resistance in series with an inductance, the latter corresponding to the induction of the measuring leads. Fig. 3 shows on the left the complex admittance plain representation of the imaginary part of the admittance (reciprocal of impedance) as a function of its real part for the assembly sample 1 – connection leads at 500K.

By exactly fitting the data calculated for the equivalent circuit to the experimentally acquired data, using Zview impedance spectra processing software [15], the Z values for the impedance of the two components of the equivalent circuit were obtained and the inductance eliminated.

The values of the admittance Y of the LSM sample, which, as indicated by the equivalent circuit, comprises only a pure ohmic component (1/R), permitted the calculation of conductivity, correcting by the form factor of the samples, following the expression:

$$\sigma = \frac{1}{R} \times \frac{l}{S},$$

where σ is the conductivity, l the thickness and S the area of the test pieces and R the electrical resistance.

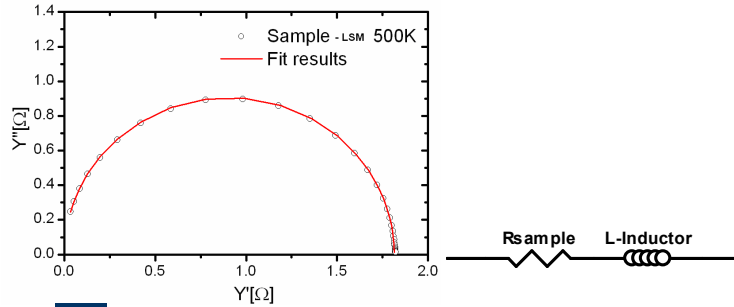


Fig. 3 Equivalent electric circuit used for impedance data interpretation.

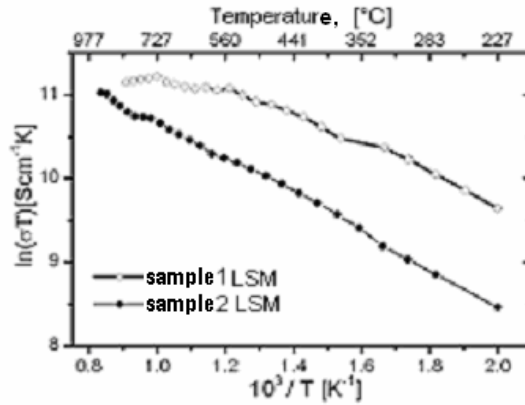


Fig. 4 Representation of conductivity as a function of temperature.

The measurement was repeated while heating each sample to a series of preestablished temperature values, and the obtained conductivity was represented in the $\ln(\sigma T) = f(1/T)$ diagrams in Fig. 4 for both investigated samples.

From the representation of electrical conductivity as Arrhenius diagrams, one observes the exponential growth of electrical conductivity with temperature, significant increase beginning with $T \sim 730^\circ\text{C}$ (Fig. 4).

This purely resistive behaviour, the high electrical conductivity values measured as well as the evolution of conductivities with temperature lead to the conclusion, that the LSM composition has a predominantly electronic conduction typical for a LSM type cathode material [9].

4. Conclusions

Based on the X-ray diffraction study performed on the LSM sample, the formation of the hexagonal type perovskite structure was established, which presents crystallisation degree and phase stability typical for lanthanum manganite based cathode type SOFC materials.

The microstructure analysis carried out by electron microscopy showed that the obtained material has a homogenous structure with well formed crystals and large pores of irregular shape, also consistent with low samples density.

At the same time, the electrical conductivity value of $\sigma = 63 \text{ S/cm}$ at $800 \text{ }^{\circ}\text{C}$ shows a behaviour typical for the crystal structure of a perovskite type ceramic material, imparting electronic electrical conductivity to it.

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