Processing and Characterization of Electrolytes Based on Doped Lanthanum Gallates for IT-SOFCs

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Abstract

Nowadays a huge interest exists towards the SOFC's coming out on the large-scale market because of the variety of their advantageous applications. Clean conversion of chemical energy to electricity, co-generation of electricity and chemicals, low levels of noise and vibration, flexibility regarding the fuels used, high efficiency are evidences of this statement.

One of the problems that still exist in this field concerns the effective and cost reasonable operation of SOFCs. In this context the lowering of the operation temperatures could be one of the solutions to this important issue.

Because of their excellent oxide-ion conductivity and stability over a broad range of oxygen partial pressure, the appropriate doped lanthanum gallates are promising alternative electrolytes for intermediate temperature SOFCs (IT-SOFCs).

The aim of this work is to present the experimental results, obtained in a close collaboration between the two Universities. The objects could be briefly outlined, as follows: to process planar electrolytes with different thicknesses, based on doped $LaGaO_3$ via traditional ceramic techniques; to study the influence of the dopants type and their amount on the properties of electrolyte materials synthesized; to investigate the phase formation and phase composition in correlation with the phase diagrams, as well as the microstructure and elements distribution. A special emphasis was placed upon the electrochemical characterization in broad temperature range, using impedance spectroscopy. The results obtained have been discussed in details and conclusions have been drawn by common efforts of the two working groups.

Introduction

The SOFC's large- scale market appearance is still representing the main challenge exciting both SOFC researchers and producers. The variety of SOFCs advantageous applications is the reason for the existing huge interest towards the opportunities that SOFC operation offers. The efforts of the scientific and industrial societies involved in this matter are focused on the attainment of effective and cost reasonable operation of SOFCs. Of course, there are a lot of things to do in this direction and plenty of problems need to be solved.

The harsh operating conditions and related to these strict requirements regarding materials, sealings, etc. result in higher SOFC manufacture costs. In this context the lowering of the operation temperature of SOFCs through use of advanced materials for device processing is one of the keys to solution of this serious issue (1, 2).

Since 1994, when the pioneering work of Tatsumi Ishihara et al. (3) was published, untill now, pronounced interest exists in the field of $LaGaO_3$ as an innovative electrolyte material for IT-SOFCs processing. Because of their excellent oxide-ion conductivity and stability over a broad range of oxygen partial pressure, the appropriate doped lanthanum gallates are really promising alternative electrolytes but unfortunately having relatively high price. That is the general reason for the restriction of their practical application. Despite this, our scientific interest has been focused on developing and study of doped $LaGaO_3$ as alternative electrolyte for IT-SOFCs. Due to the existing professional relationship between the University of Chemical Technology and Metallurgy and the University of Liège, the realization of this investigation was possible. The aim of the work is to present the experimental results obtained in a close collaboration between the two Universities.

The objects of the study could be briefly outlined, as follows: to process planar electrolytes with different thicknesses, based on doped $LaGaO_3$ via traditional ceramic techniques; to study the influence of the dopants type and their amount on the properties of electrolyte materials synthesized; to investigate the phase formation and phase composition in correlation with the phase diagrams, as well as the microstructure and elements distribution. A special emphasis was placed upon the electrochemical characterization in broad temperature range, using impedance spectroscopy. The results obtained have been discussed in details and conclusions have been drawn by common efforts of the two working groups.

Experimental Procedure and Results

The developed compositions of interest were $La_{0,9}Sr_{0,1}Ga_{0,8}Mg_{0,2}O_3$ (LSGM 10-20), $La_{0,8}Sr_{0,2}Ga_{0,8}Mg_{0,2}O_3$ (LSGM 20-20) and $La_{0,9}Sr_{0,1}Ga_{0,8}Mg_{0,15}Co_{0,05}O_3$ (LSGMC 10-15-5). The conventional solid-state route was applied for their synthesis. The raw materials were weighted and mixed in stoichiometrical ratios after that were milled together and washed with distilled water. The suspension was dried overnight at 150 °C. More details about the raw materials used, synthesis conditions, as well as for the next sintering steps are presented in the table given below.

Table 1 Experimental procedure performed trough traditional solid-state technique

Sample Composition	Raw Materials	Conditions		
		Synthesis	Pressing	Sintering
LSGM 10-20	La_2O_3 $SrCO_3$ Ga_2O_3 MgO	1300°C/6h	Uniaxially-500 kg/ inch^2 for 1min	1450 °C/2h 1450 °C/6h 1485 °C/4h in air, 200°C/h rate of heating and cooling, Pt crucibles
LSGM 20-20	La_2O_3 $SrCO_3$ Ga_2O_3 MgO	1300°C/6h	Uniaxially-500 kg / inch^2 for 1min	1450 °C/2h 1450 °C/6h 1485 °C/4h in air, 200°C/h rate of heating and cooling, Pt crucibles
LSGM 10-15-5	La_2O_3 $SrCO_3$ Ga_2O_3 $Mg(NO_3)_2.6H_2O$ $Co(NO_3)_2.6$ H_2O	1300°C/6h	Uniaxially-500 kg / inch^2 for 1min	1450 °C/2h in air, 200 °C/h rate of heating and cooling, Pt crucibles

After carrying out the stage of gallates synthesis, the samples were milled for 2 hours in planetary mill Retsch 400/2 using agate mortars and agate milling balls. Analyser Mastersizer 2000 controlled the particle size of the all powders prepared after every synthesis stage. Then the powders were shaped and pressed as discs with different thicknesses under the conditions given in Table 1. The rate of heating and cooling during the sample sintering is one parameter of a great importance and was appropriately chosen to be 200 °C/h in order to

prevent cracks formation. The sintering conditions were carefully determined after performing of some preliminary experimental steps at different temperatures and times in regard to the final density of the pellets. The recommended density of thus processed planar electrolytes required to accomplish the next measurements should be not less than 95 %. The density values of all the samples are measured to be above 95 %. As a liquid media necessary for the density measurements via the Archimedes route buthanol with density 0,81 g/cm^3 was used. Some available bibliographic data about D_{th} (theoretical density) were helpful for calculations of the parameter such as volume of open and closed porosity and apparent density for all the compositions developed.

Chemical Analysis

The synthesized perovskite powders were chemically characterized using ICP-AES analysis to verify the element content of the samples in accordance to the preliminary proposed stoichiometry.

ICP-AES analysis was performed after dissolving the powders in acids. The amounts of lanthanum and oxygen (marked with *) were not detected and their values are not presented in Table 2 below.

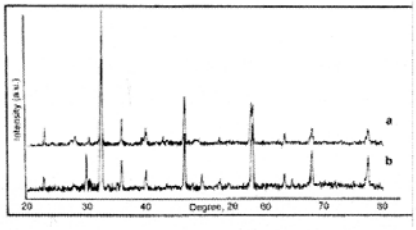
Table 2 Element content of powder samples in % based on the ICP-AES analysis

Sample	Elements, [%]					
	La	Sr	Ga	Mg	Co	O
LSGM 10-20	*	2.83	25.46	1.77	-	*
LSGM 20-20	*	5.34	24.87	3.76	-	*
LSGMC 10-15-5	*	1.63	23.19	4.01	1.45	*

Considering the results from ICP-AES analysis we can conclude that one further analysis and clarification are necessary to obtain better notion of the exact element amounts, especially in the case of gallium and lanthanum. The increased amount of gallium in comparison to the stoichiometry could be due to the detection of gallium amount along with the lanthanum amount.

Phase Formation and Composition

XRD analysis of the synthesized powders was performed using Siemens D 5000 X-Ray Diffractometer with Cu Kα radiation. Data were easy processed using XRD Evaluation Program supplied with XRD Phase Catalogue.
The results obtained are presented on figures 1, 2 and 3 for LSGM 10-20 ((a) powder sample synthesized at 1300 °C/6h and (b) after sintering at 1450 °C/6h), LSGM 20-20 ((a) after sintering at 1450 °C/2h and (b) after sintering at 1450 °C/6h) and LSGMC 10-15-5 ((a) powder synthesized at 1300 °C/6h and (b) after sintering at 1450 °C/2h), respectively.



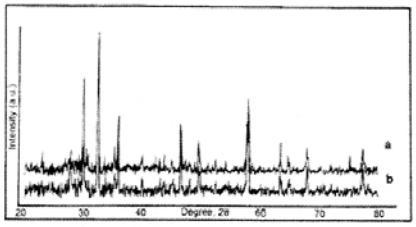


Figure 1 XRD patterns of LSGM 10-20 Figure2 XRD patterns of LSGM 20-20

On the figures presented the peaks of the main $LaGaO_3$ phase are the most intensive (detectable on the 2-Theta scale at 33, 40, 47, 53, 63, 62-63 values). In the case of LSGM 10-20 and LSGMC 10-15-5 it is clearly visible that the amounts of the secondary phases $MgGa_2O_4$ and $LaSrGa_3O_7$ are very low. This statement is confirmed also by EDX analysis performed. With increasing the temperature up to 1450 °C the amount of the supplementary phases marks a considerable increase. This tendency is observable at all the cases considered. What is more particular is that the increase of the dopants amount (in the case of LSGM 20-20) leads to an increase of the quantity of the undesirable phase $LaSrGa_3O_7$, which phase causes worsening of the overall properties and behaviour of the material synthesized. The main characteristic peaks of this phase are observable at the following 2-Theta values :23, 28, 30, 34, 35, 42, 45, at approximately 50, 60, 65, 70.

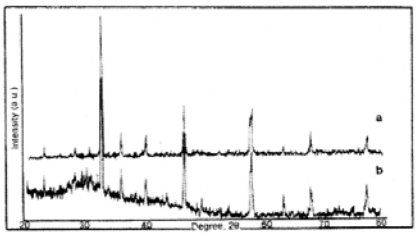


Figure 3 XRD patterns of LSGMC 10-15-5

Microstructure and Element Distribution

Microstructure and element distribution of sintered disc samples were investigated by SEM with Phillips XL30 ESEM-FED in combination with EDX analysis.

Figure 4 presents a micrograph of sample with composition LSGM 10-20 sintered at 1450 °C for 2h. What is characteristic is that the microstructure is well sintered and the average grain size varies between 1-5 μm. Accordingly to the investigated element distribution we can conclude that the perovskite phase $LaGaO_3$ predominates.

For disc samples with composition LSGM 10-20 sintered at 1450 °C for 6 h and at 1485 °C for 4 h three phases are detectable and they are common at the two sets of sintering conditions. These are namely $LaGaO_3$, $LaSrGa_3O_7$ and $MgGa_2O_4$. Their presence was confirmed clearly by XRD analysis, too.

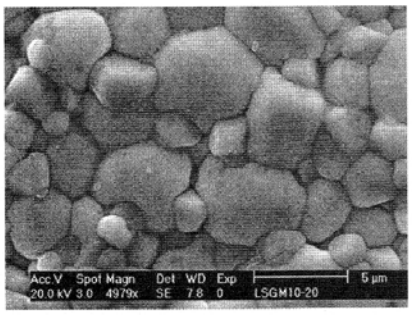


Figure 4 SEM imagine of LSGM 10-20 sintered at 1450 °C for 2h

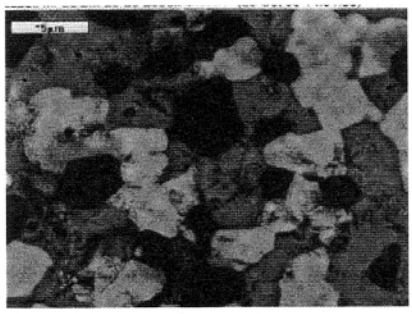


Figure 5 SEM imagine of LSGM 20-20 sintered at 1485 °C for 4h

In this case the presence of a matrix composed of $LaGaO_3$ - small grains with dimensions of 1-1,5 μm is more particular. In the matrix volume there are incorporated numerous inclusions. The larger inclusions are $MgGa_2O_4$ particles and the smaller grains are composed of $LaSrGa_3O_7$ with approximative size of 3-4 μm. We can mark also a considerable decrease of $MgGa_2O_4$ grain size to 2,5 μm, which phenomena is certainly due to the increase of the sintering time. Another interesting point is that the general amount of the inclusions in the matrix volume is not as large as in the next consideration below.

In the case of samples with composition LSGM 20-20 (Figure 5) the interpretation is similar. The observed electrolyte discs are sintered under the same conditions as the samples LSGM 10-20. Three phases are available again. They are: $LaGaO_3$ (in light grey on the micrograph) and the two undesirable phases $LaSrGa_3O_7$ (in dark grey) and $MgGa_2O_4$ (in black). Here it is not reasonable to speak about $LaGaO_3$ matrix, since accounting the amount of

the corresponding phase, it is difficult to consider it as a predominating one. This statement has found its confirmation also in the XRD results presented in the previous part, where the characteristic peaks intensities of the phases discussed give clear notion of the undesirable phase quantities.

Impedance Electrochemical Spectroscopy

In our impedance measurements Au was deposited as electrodes on both surfaces of the processed disc electrolytes by vacuum deposition. The impedance spectra of the cells with Au were measured using Solartron 1260 impedance analyzer. The thickness of all samples investigated was 2 mm. The temperature range of the impedance measurements was between 200 °C and 700 °C. On the figure below a comparison between the impedance behaviour of the developed compositions at 600 °C in air is presented. With going to the range of high frequencies, two zones are well detectable for composition LSGM 10-20: a bulk (intragrain) semicircle and an electrode-process arc, whereas the semicircle due to the grain-boundary resistance is depressed. For sample with composition LSGM 20-20 the situation is different because the second semicircle appeared, describing the grain-boundary contribution to the resistivity. It is well known that the phase $LaSrGa_3O_7$ possesses high resistance regarding the oxide-ion conductivity. Since its amount is considerable we can assume that this is the factor that determine the second semicircle appearance and larger semicircle at all. Obviously there is a segregation of $LaSrGa_3O_7$ impurities along the grain boundaries. In the case of LSGMC 10-15-5 the grain-boundary contribution is available too and it can be observed as a second semicircle. If there was detected a phase with composition $LaSrGaO_4$ it would supress the grain-boundary contribution to the oxide-ion resistivity, since this phase in a liquid state improves the grains contact during the sample sintering.

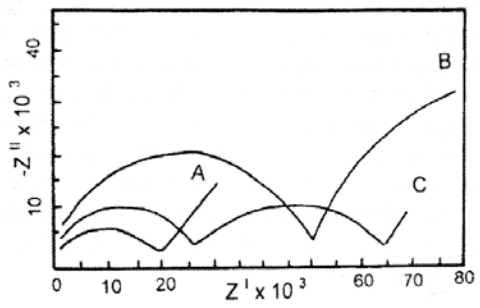


Figure 6 Comparative Impedance Spectra of LSGM 10-20 (A), LSGM 20-20 (B) and LSGMC 10-15-5 (C) at 600 °C

Conclusions

On the basis of the study performed we can summarize that it is difficult to obtain single-phase product via solid-state reaction as a method of synthesis. Since Ga is volatile it is possible definite losses to be detected during the sintering stage. It is known that even the slightest changes in Ga content can reflect on the phase formation and phase composition of the samples synthesized, as well on the sintering behaviour, morphology and the electrical conductivity. Since we did not detected $LaSrGaO_4$ phase, we suggest that the evaporation of Ga is not in a large extent. In this sense the presence of $LaSrGaO_4$ is dangerous because it becomes liquid during the sintering stage and in this way it is easier some Ga to be evaporated.

The presence of $LaSrGa_3O_7$, especially in the LSGM 20-20 in such a large amount is emphatically undesirable since it possesses bad conduction characteristics with respect to the oxide-ion conductivity. It appears to be difficult to give an explanation why this phase was detected in such amount only in LSGM 20-20 especially if we consider that the Ga content in the samples with compositions LSGM 10-20 and LSGM 20-20 is stoichiometrically the same. If the Ga amount were different in the two compositions, the appearance of Ga-enriched phase $LaSrGa_3O_7$ would not be so suspect.

Relying on the results from XRD, SEM, EDX and Impedance Spectroscopy we can conclude that the samples with composition LSGM 10-20 possess homogeneous microstructure and even if the other two phases $LaSrGa_3O_7$ and $MgGa_2O_4$ were available their content is small. The bulk resistance of LSGM 10-20 in comparison with the other compositions investigated is the smallest one. The lack of grain-boundary semicircle is indicative and shows that any segregation of impurities along the grain boundaries can be detected. With regard to the microstructure of the samples we can conclude that they are well sintered with a homogeneous microstructure. The densities measured confirm this statement. In the case of LSGM 20-20 both bulk and grain-boundary resistances are well expressed. We can interpret the bulk resistance as a result of the large amount of impurity phases ($LaSrGa_3O_7$ and $MgGa_2O_4$) observable as well detached impurity grains in the matrix of the main phase. The grain-boundary resistance is due to the impurity segregation along the grain boundaries. In order to clarify completely the possible reasons for the origin of the impurities detected additional investigations are necessary to be performed in this direction. Moreover this important issue could be marked as one next trend for our future investigations.

Acknowledgements

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