Correlations Composition - Processing - Microstructure - Properties for Ceria - Based Solid Electrolytes

ZENO GHIZDAVET¹, IULIANA MADALINA STANCIU^{1,2*}, ALINA MELINESCU¹, ADELINA IANCULESCU¹

¹University Politehnica of Bucharest, Department of Science and Engineering of Oxide Materials and Nanomaterials, 1-7 Gh. Polizu Str., 011061, Bucharest, Romania

²Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, 30 Reactorului Str., 077125, Magurele, Ilfov, Romania

The main objective of this work is to study the correlation between composition, microstructure, processing and properties of doped ceria. Doped ceria with heterovalent cations can be used as solid electrolyte for solid oxide fuel cells working at intermediate temperatures (SOFC-IT). This study is made in order to obtain information, which can be useful for further improvement of this type of materials. Multivariate analysis techniques, such as Principal Component Analysis (PCA) and Self-Organizing Maps (SOMs) were used on a database consisting of 18 samples which differ by composition and by processing methods. Experimental data regarding these samples consisted in information about composition, SEM images and the property of choice, the electrical conductivity. SEM images were digitally processed to isolate grain boundaries; on the 18 resulting images it was computed the Fractal Dimension, as a parameter containing both information about size and shape of the grains, therefore characterising the microstructure. All results were, then, subjected to Multivariate analysis taking into account, also, the processing methods. The aim is to extract useful information from the available experimental data. Results encourage us to assume that even identification and diagnose can become possible based on the present work, given an adequate database. The overall procedure can be applied to any crystalline material.

Keywords: doped ceria, solid electrolyte, image analysis, multivariate analysis, fractal dimension

Correlations within parts or even on the entire chain composition, microstructure, processing, properties are mandatory in materials science, for obvious reasons. Correlations can be obtained i) by an empirical analysis of the results or ii) by using various computational [analysis] techniques [1-3]. In case i), the success of the analysis depends on the experience of the research team; however, comparisons can become, in some cases, subjects to long and unproductive debates as the process of extracting the information depends on particular experiences. On the other hand, case ii) offer a common platform for analysis and interpretation. Nowadays, computational methods allow to design a material at all scales; multiscale modelling would be highly desirable to tailor material properties. The main drawbacks – except for the built in issues, for example the selection of a particular approach in ab initio methods or a specific potential and so on to mesoscale and macroscale modelling - are their computational costs and their specificity. Hence, the need to use techniques and methodologies that are both simple and effective and can include also experimental results within their overall workflow. In this paper, it was developed such a methodology.

One of the representative electrolyte materials for a high temperature solid oxide fuel cell is zirconia-based oxide because of its attractive ionic conductivity. If lower temperatures are to be considered, the ionic conductivity of ceria-based oxide is higher than that of zirconia-based electrolytes. As lower working temperatures are desired nowadays, ceria-based oxide was found to be a promising material in order to function as a solid electrolyte [4-7].

Samarium or gadolinium doped ceria in literature had been reported to provide the highest electric conductivities among the family of ceria doped materials; the explanation lies in the relationship between the ionic radius of the dopant used and the cation ionic radius of the host lattice [8-10]. In his work, Kim [11] proposed a critical ionic radius for the dopant, which would give the same lattice constant as that of the electrolyte without any additive in his structure. But, according to Kilner et al. and Catlow [12, 13] a smaller difference between the ionic radius of the host and the dopant is preferable for obtaining a high conductivity, because this way the lattice will keep its symmetry.

Improving performance of solid oxide electrolytes mean to increase the ionic conductivity of the ceria-based electrolytes [14]. Understanding the various factors that influence ionic conductivity can help to optimise the properties of doped ceria.

In this paper, the effects in terms of composition, microstructure, and processing on the properties for ceriabased electrolytes are studied. With this purpose in mind, there were used 18 different types of samples in terms of the factors listed above. These factors are fully related to each other as shown in figure 1.

Various compositions and several processing methods were considered in order to get a wider picture of the correlations between all these factors. Compositional features (such as atomic percentages of Ce, lattice parameter) and all processing methods and conditions



Fig. 1. Correlations composition, processing, microstructure and properties

were known for 18 different samples. Two main ideas were considered in constructing this paper: a) the methodology has the most importance; b) experimentals have to be different and available in a large number. Referring to point b), as a consistent database was needed (made of wideranging combinations of compositional features and processing methods that lead to an important volume of results), reported data were used [15-20]. Specific image analysis techniques were used to define and isolate grain boundaries on SEM images of the materials. Once the contours were isolated, Fractal Dimension (FD) was computed on the resulting images; FD was intended to describe microstructural features. Electric conductivity was selected as property. All these quite different parameters were then analysed by PCA and SOMs techniques, by using the processing method as criterion for classification. Patterns of correlations between parameters and similarities between samples were extracted; they explain and support by analysis our expectations. Score plots reveal that samples were grouped in distinct clusters, allowing the identification of the influence of various parameters; the most important finding was that each processing method has its own projection space on the two Principal Components. The consequence is that, based on this methodology one can even identify or diagnose, provided a relevant database is supplied and regardless the material. Our recent results on using this methodology (with some variations in the selection of the parameters, due to the inner specificity) on another material - cement clinker - that is interesting for its mechanical properties, confirmed the reliability of the method.

The ionic conductivity of electrolytes can be maximized by properly altering composition; this can be done by selecting an appropriate heterovalent dopant and its optimal concentration.

Ceria has a fluorite-type structure, which remains stable from room temperature to its melting point ~2400°C. At temperature of 1300°C, part of Ce⁴⁺ ions are reduced to Ce³⁺, to form anionic vacancies. However, despite this fact, pure CeO₂ do not provide significant ionic conductivity. In order to achieve high ionic conductivity, oxygen vacancies are to be created into the structure via substitution of host Ce⁴⁺ by acceptor cations.

The ionic conductivity reaches a maximum at dopant concentration of about 10-20 mol. % depending on the type of dopant. This phenomenon is typically associated with the interactions of oxygen vacancies with dopant cation, and forms local defect structures. The conductivity is further influenced by the size of dopant, binding the energy of the oxide ion with the host cation and migration enthalpy of the mobile ions [21].

Processing conditions are another area that can greatly influence the electrical conductivity of electrolytes. These include different sintering processes in order to prepare ceramics with a controlled microstructure (grain size, density). Different sintering conditions will result in diverse characteristics in the microstructures of the electrolyte such as grain size, grain boundary phases, and phase segregation on the boundaries, agglomeration, and relative density.

The ionic conductivity varies strongly with the sintering conditions of the electrolyte, for example it was observed the high values of grain boundary resistance at sintering temperatures below 1300°C due to the low relative density of the electrolyte, also, was observed the linear correlation between grain boundary conductivity and porosity. A microstructure with a relative density greater than 90% is therefore an essential requirement for a high-performance ionic conductor [22].

The samples used in this paper were obtained both through conventional method (solid-state reaction) and unconventional methods (sol-gel, coprecipitation, Pechini, hydrothermal).

The total ionic conductivity of a polycrystalline electrolyte depends upon the contribution from both grain and grain boundary.

The first zone is within the grains, which is the zone of high ionic conduction, and is separated by poorly conducting, thin grain boundaries. Due to positive spacecharge at the grain boundaries, oxygen vacancies and holes positive charge carriers) are depleted, while the electrons or acceptor dopants are accumulated near the grain boundary region. The increase of the temperature lead to a reduction of the grain boundary resistance; the temperature at which the grain boundary blocking effect becomes negligible is dependent on the dopant concentration.

In order to analyse the microstructure of a polycrystalline material it was used Scanning Electron Microscopy (SEM); SEM images obtained provide a qualitative analysis. In order to integrate SEM images in a multivariate analysis it needs to be defined by a numeric value, so it was calculated the fractal dimension (FD) [23]. This parameter has been chosen as containing simultaneously shape information and size of the particles (but not for the fractal nature of the grains). Calculation of fractal dimension can be done by Richardson method or the method of counting boxes (box-counting). In this paper it was used the second method, i.e. box-counting [24].

Experimental part

The synthesis of solid electrolytes we deal with in this paper has been done by various methods, both conventional (solid-state reaction) and unconventional (sol-gel, coprecipitation, hydrothermal, Pechini).

SEM images corresponding to 18 different samples were digitally processed in order to detect and isolate grain boundaries. On resulting images, fractal dimension were computed. [Note: Fractal dimension was not intended here to address a possible self-similarity of the grain contour. Instead, FD was used because it provides a single value that can be further processed to extract correlations; it is also useful because it includes information about both shape and size of the grains and, if it is the case, about the texture. Moreover, grains placed at the edges of the SEM or optical microscopy images do not have, typically, closed contours, thus being useless to obtain other parameters (equivalent diameters, shape factors etc.). The database concerning composition, processing conditions, microstructure and properties was further analysed by PCA-Principal Component Analysis and SOM-Self Organizing Maps methods. These methods can be used when dealing with parameters of different nature and of various orders of magnitude, on complex databases concerning diverse fields of application [25] for more information and results on these methods). Results were interpreted in terms of extracting information. It is considered that such a study, involving multivariate analysis methods can contribute to the development and optimization of ceria-base electrolytes, furthermore, the overall methodology can be applied to any polycrystalline material with virtually no modification.

The value of fractal dimension is given by the shape and the grain size as well as irregularities of the grain boundaries. The procedure is shown schematically in figure 2 and is described in steps in the next section.



Edge Detection techniques were employed to identify and isolate grain boundaries in SEM images (fig. 2). In short, SEM images were processed within ImageJ environment: images were digitized and various filters were applied: Threshold, Edge Detection, Erode/Dilate. Threshold values were selected specifically on each image. On the resulting images containing only grain boundaries, Fractal Dimension (FD) has been computed, also in ImageJ by covering the image with a grid, and then count how many boxes of the grid are covering part of the microstructure. Then it does the same thing but using a finer grid with smaller boxes. By shrinking the size of the grid repeatedly, it ends up more accurately capturing all the microstructure. Using the box counting method, fractal dimension is the slope of the line obtained by plotting the value of log (counts) on the Y-axis against the value of log (box size) on the X-axis. Counts defines the number of boxes that covers the grains boundaries, and the box size is the dimension of the boxes used for each magnification of the grid.

Results and discussions

Before processing the images, it was tested whether the image size, expressed as the area which includes a different number of grains on which is performed the calculation, influences the value of fractal dimension.



Fig. 3. FD values depending on the number of grains in a given image

Df=1.4442 (Area=52%)

After applying the procedure sketched in figure 3 it was found that the value of fractal dimension for all areas considered (different numbers of grains) does not change significantly, the difference is at the 3-digit after the decimal point. As a consequence, it was inferred that magnification scale of the SEM result will have a very small impact on the results.

For all SEM images it was computed the Fractal Dimension, FD. The samples used have different compositions and various methods of processing, and heat treatments were carried out at various temperatures.

In this paper, the fractal dimension of a microstructure do not express the self-similar feature of the grain boundary, it just defines grain size and shape and irregularity of grain boundaries (if there is any).

Table 1 collects all 18 samples of different ceria-doped materials with their grain boundaries on which it was computed the FD, according to the procedure sketched in figure 2.

These types of microstructures, well densified, are obtained by both conventional and unconventional methods, conventional ones are characterized by sintering

Fig. 2. Fractal Dimension (FD) obtaining procedure from SEM images

 Table 1

 SEM IMAGES, GRAIN BOUNDARIES AND FD VALUES USED FOR CORRELATION Remark: processed SEM images were obtained at various

magnifications

Sample	CeO2 solid solution	Grain boundaries	FD
E1	$Ce_{0.87}Sr_{0.09}Y_{0.04}O_{2-\delta}$	Table 1. Fig. 1	1.3697
E2	$Ce_{0.8}Sm_{0.2}O_{2-\delta}$	Table 1. Fig. 2	1.3311
E3	$Ce_{0.8}Ca_{0.2}O_{2-\delta}$	Table 1. Fig. 3	1.5604
E4	$Ce_{0.85}Ca_{0.15}O_{2-\delta}$	Table 1. Fig. 4	1.5027
E5	Ce _{0.95} Ca _{0.05} O _{2-ô}	Table 1. Fig. 5	1.5259
E6	$Ce_{0.8}Ca_{0.05}Sm_{0.15}O_{2-\delta}$	Table 1. Fig. 6	1.5870
E 7	$Ce_{0.8}Sr_{0.05}Sm_{0.15}O_{2-\delta}$	Table 1. Fig. 7	1.4759
E8	$Ce_{0.9}Nd_{0.05}Sm_{0.05}O_{2-\hat{\sigma}}$	Table 1. Fig. 8	1.4880



time of more than 4 hours, or additional heat treatments, because usually the grains of raw materials are micrometre scale. Instead, for unconventional methods long sintering time are not necessary because the grains of obtained powders are nanometre scale with high specific surface, this way the reactivity is high and the heat required for the reactions to occur is lower.

Fractal dimension values were found to be in the range 1.306 and 1.587; minimum values are for samples with large grain size and high densities, otherwise, high values are characterizing the fine-grained samples with low densities.

PCA analysis is a good candidate when an analysis deals with many influencing factors, which can be very different in nature, orders of magnitude and units, and normally cannot be explained by analyzing two-dimensional plots. Thus, this method allows representation of data (which should be in multidimensional space, which is impossible) in two-dimensional space through two Principal Components.

Influencing factors considered here are:

-the lattice parameter (a [Å]) that includes the changes made by dopant in the crystal structure and the influence of the processing method.

- processing methods (M) of the samples used to analyse various factors that influence the ionic conductivity are unconventional (M1) Sol-gel: E9, E10, E11 [16], (M2) Coprecipitation: E12, E13, E14, E15, E16 [17], (M3) hydrothermal: E17 [18], (M4) Pechini: P18 [19], and conventional (M0) solid-state reaction: E1, E2 – our own samples, E3, E4, E5, E6, E7 - [15], E8 [20]. Also, the processing methods include: presintering/calcination temperature (T1 [°C]), the sintering temperature (T2 [°C]) and sintering time (St [h]).

- the microstructure is defined by the fractal dimension (FD), a dimensionless parameter which contains information about grain size and shape.

- total electrical conductivity (σ ·10⁻² [S·cm⁻¹]) measured at 600°C, which is the property of choice for a solid electrolyte.

Also, for PCA analysis it was used the atomic percentage of cerium (Ce [at. %]) from the solid solutions considered.

Table 2 contain the centralized data of various factors that influence ionic conductivity necessary for analysis; the aim is to reveal correlations composition – processing – microstructure – properties.

PCA analysis was performed on two data sets, Data Set 1 (all parameter values) and Data Set 2 (without lattice parameter values), in order to make a comparison between results.

In both cases, PCA analysis performed on parameter values (fig. 4), indicates the importance of the type of method used (conventional or unconventional) and the temperatures at which heat treatments were performed. This is evidenced by the proximity on the Principal Component 1 axis (which explains 51.9% of the variance of the data) and especially the value that it takes on the respective Principal Component. By comparing the two plots, it can be observed, when lattice parameter values are used, that the Loadings plot is slightly altered. From these findings, it resulted that lattice parameter *a* is not an influential parameter. Lattice parameter is known to be dependent on the nature and concentration of the dopant; it was rejected for now but it should be further studied exactly how influential it is, maybe in another combination of parameters.

Also, it can be noticed the opposite behaviour of atomic percentages of cerium and conductivity over PC2. This

Sample	Ce [at. %]	a [Å]	М	T1 [°C]	T2 [℃]	St [h]	FD	σ · 10 ⁻² [S·cm ⁻¹] (600°)
E1	0.87	5.4181	0	0	1400	3	1.3697	0.8200
E2	0.8	5.4320	0	1300	1550	4	1.3311	0.9600
E3	0.9	5.4170	0	1300	1550	4	1.5604	0.8700
E4	0.85	5.4160	0	1300	1550	4	1.5027	0.7300
E5	0.8	5.4270	0	1300	1550	4	1.5259	1.5300
E6	0.8	5.4300	0	1300	1550	4	1.5870	1.2200
E7	0.8	5.4380	0	1300	1550	4	1.4759	1.1300
E8	0.9	5.4190	0	1450	1550	10	1.4880	1.2800
E9	0.8	5.4370	1	600	1500	4	1.4464	0.0200
E10	0.8	5.4470	1	600	1500	4	1.3064	0.0284
E11	0.8	5.4420	1	600	1500	4	1.2960	0.1323
E12	0.8	5.3970	2	600	1500	5	1.4447	0.7400
E13	0.8	5.4280	2	600	1500	5	1.4445	1.5900
E14	0.8	5.4330	2	600	1500	5	1.4309	0.5900
E15	0.8	5.4410	2	600	1500	5	1.3792	1.2900
E16	0.8	5.4750	2	600	1500	5	1.3016	0.9600
E17	0.8	5.4290	3	0	1350	5	1.4770	0.7940
E18	0.78	5.4270	4	900	1500	2	1.3769	0.4700

 Table 2

 CENTRALIZED DATA TO BE USED IN THE ANALYSIS





behaviour is due to the concentration of vacancies formed by replacing cerium with different dopants. Thus, when cerium is replaced by an excessive amount of divalent or trivalent cations, clusters are formed, though inducing bidimensional defects in structure. These ones affect in a negative way the migration of oxygen ions; if it is too low, it doesn't form a sufficient number of vacancies in order to ensure a high ion conductivity.

The total conductivity and sintering time are located in the same area, so it can be expected that there is a relationship between them. When the samples are kept for a longer time at the given temperature, the grains are increasing in size, the fractal dimension decreases and conduction occurs mainly within grains (and less contribution can be attributed to grain boundaries conduction); overall, the total conduction increases. It can be concluded that π is strongly influenced by St. viewed as groups of parameters, the group (σ and St) has a negative correlation to the group (Ce and FD).

The processing temperatures present an opposite behaviour to fictional method index (the numerical value is not important here – it only denotes the methods). For example, when the method has the lowest index, which is



0 (solid-state reaction method) the processing temperatures are higher than the temperatures required for *wet* methods, because the powders obtained by unconventional methods are nanometric scale (in this cases it is not necessary a high temperature for the reactions and densification to work).

By analysing figure 5, it can be seen that samples are automatically grouped corresponding to each processing method. Score plots will be further correlated with Loadings.

Along PC1 the most influential parameters are T1 and T2. Among all results these 2 parameters have the most of the influence over the materials obtained by the conventional method M0 (which was to be expected). Parameters T1 and T2 less influence the results when M3 processing conditions are used (M3 – hydrothermal method, in this case the sample did not required a presintering or calcination treatment before sintering and the temperature of sintering (T2) was 1350°C, which was the lowest one of all).

In figure 5 a, clusters corresponding to methods M1, M2 and M4 overlap at a certain extent; this could be explained by the fact that, although the materials were obtained using different dopants and different concentrations, the lattice parameters have similar values for some of these materials. By eliminating the lattice parameter a from analysis, the clusters become distinct (fig. 5 b).

M0 group of samples lays along the entire PC2. An interesting interpretation can be made by considering the influence of the conductivity. When correlating with the loadings plot (fig. 4) it can be observed that two samples are characterized by very high values of conductivity, the other two (in the lower part) have very small values, another two samples are placed on the horizontal axis of

PC1, where average values are to be found and the other two have relatively high values.

Self-Organizing Maps (SOMs) analysis has been made, also, and the results are shown in figure 5.

The results of SOMs analysis validate at a certain extent the results of the PCA method. The method of synthesis, *M*, and heat treatment temperatures (*T1* and *T2*) are well correlated, and this correlation can be easily seen. The two heat treatment temperatures have similar behaviours while being opposite to the processing method.

The other parameters cannot be related to each other by using this method, but partially. To achieve better results with this method, the number of records (samples) should be increased.

Conclusions

The main objective was to study the correlations between composition, processing, microstructure and properties by means of multivariate analysis methods (Principal Component Analysis and Self Organizing Maps).

In this regard, we used 18 data sets that have a wide range of compositions, with different combinations of dopants, methods of processing (both conventional and unconventional), various heat treatment temperatures, and different resulting microstructures.

Relationships between parameters and similarities between records were extracted and explained, from both structural and experimental viewpoints (different processing conditions lead to different microstructures).

Microstructure features, such as grain size and shape were quantified by computing the fractal dimension (*FD* was not used here for assessing the fractal nature but as a parameter). The procedure used here can be easily ported to any other polycrystalline material. Results can be used for identification or diagnose of an unknown or partially unknown polycrystalline material; this inference can be founded on the fact that score plots in PCA revealed a good separation of the records in distinct clusters concerning materials obtained by different methods.

PCA was performed using the Excel add-in Multibase package (Numerical Dynamics, Japan). SOM analysis was performed using Peltarion Synapse. Image analysis has been made by using ImageJ tools.

References

1.GHIZDAVET, Z., Rev. Chim. (Bucharest), **57**, no. 5, 2006, p. 537. 2.GHIZDAVET, Z., RADU, D., Rev. Chim. (Bucharest), **56**, no. 12, 2005,

2. GHIZDAVEI, Z., RADU, D., Rev. Chim. (Bucharest), **56**, no. 12, 2005, p. 1214.

3.RADU, D., GHIZDAVET, Z., Rev. Chim. (Bucharest), **58**, no. 7, 2007, p. 677.

4.KHARTON, V.V., MARQUES, F.M.B., ATKINSON, A., Solid State Ionics, **174**, no. 1-4, 2004, p. 135.

5.ISHIHARA, T., TABUCHI, J., ISHIKAWA, S., YAN, J., ENOKI, M., MATSUMOTO, H., Solid State Ionics, **177**, no. 19-25, 2006, p. 1949.

6.SAMMES, N.M., TOMPSETT, G.A., NAFE, H., ALDINGER, F., J. Eur. Ceram. Soc., **19**, no. 10, 1999, p. 1801.

7.MINH, N.Q., TAKAHASHI, T., Science and Technology of Ceramic Fuel Cells, Elsevier, Amsterdam, 1995.

8.INABA, H., TAGAWA, H., Solid State Ionics, 83, no. 1-2, 1996, p. 1.

9.EGUCHI, K., SETOGUCHI, T., INOUE, T., ARAI, H., Solid State Ionics, **52**, no. 1-2, 1992, p. 165.

10.YOSHIDA, H., DEGUCHI, H., MIURA, K., HORIGUCHI, M., INAGAKI, T., Solid State Ionics, **140**, no. 3-4, 2001, p. 191.

11.KIM, D.J., J. Am. Ceram. Soc., 72, 1989, p. 1415.

12.KILNER, J.A., BROOK, R.J., Solid State Ionics, **6**, no. 3, 1982, p. 237. 13.CATLOW, C.R.A., Solid State Ionics, **12**, 1984, p. 67.

14.VELCIU, G., MELINESCU, A., MARINESCU, V., FRUTH, V., SCURTU,

R., PREDA, M., Rev. Rom. Mater., **44**, no. 2, 2014, p. 131.

15.WU, Y., LIN, C., Int. J. Hydrogen Energy, 39, no. 15, 2014, p. 7988.

16.LI, S.P., J.Q. LU, FANG, P., LUO, M.F., J. Power Sources, **193**, no. 1, 2009, p. 93.

17.FU, Y.P. CHEN, S.H., HUANG, J.J., Int. J. Hydrogen Energy, **35**, no. 6, 2010, p. 745.

18.DIKMEN, S., ASLANBAY, H., DIKMEN, E., J. Power Sources, **195**, no. 9, 2010, p. 2488.

19.DUDEK, M., Int. J. Electrochem. Sci., 7, no. 4, 2012, p. 2874.

20.OMAR, S., WACHSMAN, E. D., NINO, J. C., Solid State Ionics, 178, no. 37-38, 2008, p. 1890.

21.MAHATO, N., BANERJEE, A., GUPTA, A., OMAR, S., BALANI, K., Review, Prog. Mater. Sci., 72, 2015, p. 141.

22.GIBSON, I.R., DRANSFIELD, G. P., IRVINE, J. T. S., J. Mater. Sci., 33, no. 17, 1998, p. 4297.

23.OLTEANU, M., PAUN, V.P., TANASE, M., Rev. Chim. (Bucharest), 56, no. 1, 2005, p. 97.

24.GHIZDAVET, Z., REHNER, H., Building materials, **4**, 2000, p. 303. 25.GHIZDAVET, Z., Rev. Rom. Mater., **40**, no. 1, 2010, p. 161.

Manuscript received: 30.03.2016