

PHASE TRANSITIONS IN $ZrO_2:La_2O_3$ SOLID ELECTROLYTES.

R. MUCCILLO, Y. V. FRANÇA

Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear,
C.P. 11049-Pinheiros, CEP 05422-970, S. Paulo, S.P., Brazil.

ABSTRACT

$ZrO_2:m$ mol% La_2O_3 ($m=10, 15, 20, 33$) ceramic powders have been prepared by the citrate method and analyzed by X-ray sedimentography, X-ray Diffractometry and Scanning Electron Microscopy. The lanthanum content was determined by thermal neutron activation and High Performance Liquid Chromatography methods. The powders have been pressed and sintered at $1550\text{ }^\circ\text{C} / 1\text{ h}$. Impedance spectroscopy (IS) measurements have been carried out in the 5 Hz - 13 MHz frequency range in the $500\text{ }^\circ\text{C} - 800\text{ }^\circ\text{C}$ temperature range in sintered specimens and also during sintering green ceramics up to $1350\text{ }^\circ\text{C}$. Differential thermal analysis (DTA) have also been performed in the powders in the same temperature range. The main results show evidences of correlations between IS and DTA data, allowing for the tetragonal-to-pyrochlore phase transition detection in $ZrO_2:La_2O_3$ solid electrolytes.

(zirconia, solid electrolyte, impedance spectroscopy)

INTRODUCTION

Ceramic oxide solid electrolytes are widely used as electrochemical transducers in oxygen sensors. The most common oxides that behave as oxygen-ion conducting solid electrolytes are $ZrO_2:Y_2O_3$, $ZrO_2:CaO$, $ZrO_2:MgO$ and ZrO_2 stabilized with rare earth oxides [1]. Sensors of this kind can be used in a variety of applications: for monitoring oxygen dissolved in molten steels, for detecting oxygen compounds in automotive exhaust tubes helping pollution control and regulation of fuel consumption, for detecting oxygen in industrial gases, etc. In all cases the electrochemical transducers are ZrO_2 -based solid electrolytes [2, 3]. There are basically two ways for preparing ceramic solid electrolytes: a) simply mixing the proper amounts of the stabilizing agent (MgO , Y_2O_3 , rare earth oxides) to ZrO_2 , pressing and sintering at high temperatures and b) following one of a variety of chemical solution techniques. The advantages of the latter are that the powders exhibit improved chemical homogeneity and higher reactivity than the ones by the

RESUMO

Pós cerâmicos de $ZrO_2:m$ mol% La_2O_3 ($m=10, 15, 20, 33$) foram preparados pelo método dos citratos e analisados por meio de sedimentografia de raios X, difratometria de raios X e microscopia eletrônica de varredura. O teor de lantânio foi determinado por análise de ativação neutrônica e por cromatografia líquida de alto desempenho. Os pós foram prensados e sinterizados a $1550\text{ }^\circ\text{C} / 2\text{ h}$. Medidas de espectroscopia de impedância foram feitas na faixa de frequências de 5 Hz a 13 MHz, entre $500\text{ }^\circ\text{C}$ e $800\text{ }^\circ\text{C}$ em amostras sinterizadas e também durante a sinterização até $1350\text{ }^\circ\text{C}$ de compactados à verde. Análise térmica diferencial também foi feita nos pós na mesma faixa de temperaturas. Os principais resultados mostram evidências de correlação entre os dados de Espectroscopia de Impedância e de Análise Térmica diferencial, permitindo a detecção da transição de fase tetragonal-pirocloro nos eletrólitos sólidos de $ZrO_2:La_2O_3$.

(zircônia, eletrólito sólido, espectroscopia de impedância)

conventional mixed oxide process, enabling sintering to high densities at relatively lower temperatures. Amongst the solution techniques, the one that yields an amorphous organic resin that can be converted to homogeneous solid solution oxides upon heating is the citrate method [5]. In this work, the synthesis of $ZrO_2:La_2O_3$ powders by the citrate method is described. The powders, after characterization by X-ray diffractometry (XRD) at room temperature for phase identification, sedimentographic measurements for determination of agglomerate particle distribution, and HPLC analysis for La content determination, were pressed to pellets and sintered at $1550\text{ }^\circ\text{C}$ for microstructure characterization by XRD, neutron activation analysis for determination of La content and electrical characterization by impedance spectroscopy. *In situ* impedance spectroscopy analysis has also been done by measuring ac responses in the 5 Hz - 13 MHz frequency range during sintering green compacts in a specially designed spring-loaded sample chamber.

EXPERIMENTAL

The raw materials used were BDH zirconyl chloride, 99.6 % pure Sigma lanthanum oxide, citric acid (99.5%) and concentrate nitric acid both from Merck, and P.A. ethylene glycol. La_2O_3 - stabilized ZrO_2 powders were prepared by the citrate method [5]. That method consists essentially in mixing salts to citric acid and to ethylene glycol at suitable temperature baths to obtain a polymeric resin that after heating results in a reactive powder. Here zirconyl chloride is added to lanthanum chloride, heated up to 90 -100°C, followed by additions of citric acid, ethylene glycol and nitric acid under continuous stirring. The resin then obtained is calcined at 1000 °C for 2 hours yielding fine $\text{ZrO}_2\text{:La}_2\text{O}_3$ powders. Average agglomerate particle size distribution measurements have been done in a Micromeritics 5100 Sedigraph Analyzer. The HPLC technique (Waters 625 LC system) has been used for the determination of La content. Pressed powders were sintered at 1550 °C in a Lindberg super-kanthal furnace. The densities of pressed pellets were determined by the Archimedes method (immersion in water). Phase identification of sintered pellets was done by X-ray diffraction at room temperature in a PW3710 Philips diffractometer using $\text{Cu-K}\alpha$ radiation. The lanthanum content in the ZrO_2 pellets has been determined by thermal neutron activation analysis. Impedance spectroscopy measurements were carried out in the 5 Hz - 13 MHz frequency range with a Hewlett Packard 4192A LF impedance analyzer connected via HPIB to an HP 900 controller, in the 300 °C - 650 °C temperature range, using an inconel 600 and alumina sample chamber with a Pt-Pt10%Rh thermocouple for temperature monitoring. In situ impedance spectroscopy studies have been performed in the 500 °C - 1350 °C temperature range. An all high-alumina/Pt sample chamber has been built to be inserted in a tubular furnace. Pt electrodes were applied to the planar opposite surfaces of cylindrical pellets by sputtering under argon gas or by painting with Demetron 308 Pt paste. Netsch DTA-TGA 409 and dilatometer 402 E/7 have been used for differential thermal and dilatometry analyses, respectively, in the RT-1400 °C range with a 10 degrees/min heating rate.

RESULTS

ZrO_2 : m mol% La_2O_3 (m=10, 15, 20 and 33) powders have been prepared following the citrate route described above. Sedigraphic analysis of the powders obtained by the citrate method allowed for the determination of average particle sizes in the 0.7-1.1 μm range. High Performance Liquid Chromatography measurements in some powders, after continuous

dilution in Pt crucibles, gave the values shown in Table I.

Table I: Values of La_2O_3 added to ZrO_2 and determined by High Performance Liquid Chromatography.

nominal La_2O_3 mol %	nominal La_2O_3 wt %	HPLC La_2O_3 wt %
10	22.7	19.4
15	31.8	32.9
33	56.6	51.3

The determination by HPLC of La_2O_3 content in $\text{ZrO}_2\text{:La}_2\text{O}_3$ ceramic powders prepared by the citrate method shows that there are not large losses of the stabilizing oxide following that chemical procedure. The determination of lanthanum content in $\text{ZrO}_2\text{:La}_2\text{O}_3$ sintered pellets by neutron activation analysis was in agreement with the determination by HPLC in precursors powders.

In Fig. 1 X-ray diffraction results of $\text{ZrO}_2\text{:15 mol\% La}_2\text{O}_3$ powders obtained by the citrate method are shown for the 20 °- 40 ° 2θ range. In the same figure is also shown the diffractogram of the same powder after pressing and sintering at 1650 °C/1 h. The powder has two main diffraction lines for $2\theta = 29^\circ$ and 33.6° , due to the tetragonal phase according to Bastide, Odier and Coutures [6]. The sintered pellet, on the other hand, shows several additional diffraction lines due to the tetragonal-to-pyrochlore phase transition known to occur after annealing tetragonal ZrO_2 : m mol% La_2O_3 ceramics for m greater than 2 [6].

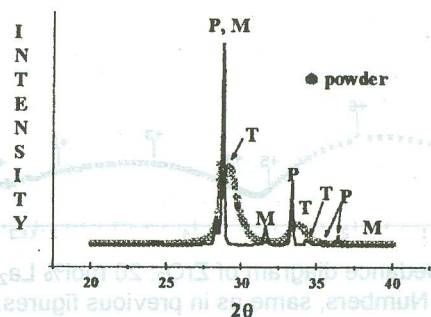


Fig.1: X-ray diffractogram of ZrO_2 : 15 mol% La_2O_3 powder and sintered pellet. M, T and P are monoclinic, tetragonal and pyrochlore lines, respectively.

Figs. 2, 3 and 4 show Nyquist diagrams of the sintered pellets of ZrO_2 :10 mol % La_2O_3 , ZrO_2 :15 mol % La_2O_3 and ZrO_2 :20 mol % La_2O_3 , respectively, measured at 550 °C.

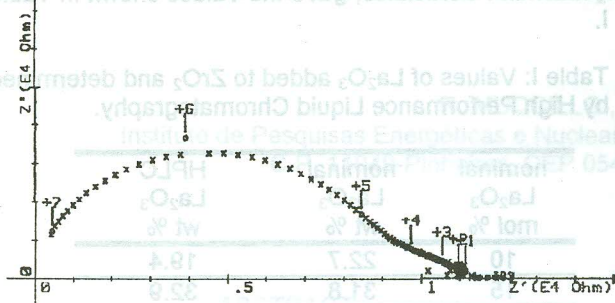


Fig. 2: Impedance diagram of ZrO_2 : 10 mol% La_2O_3 at 550 °C. Numbers are logarithm of frequency.

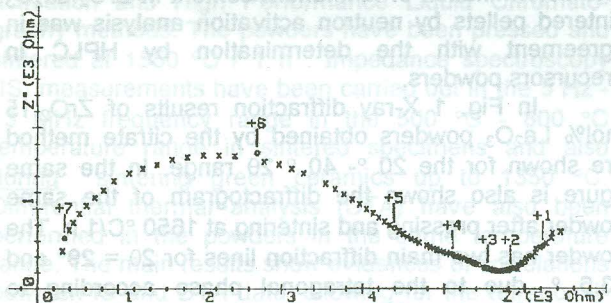


Fig. 3: Impedance diagram of ZrO_2 : 15 mol% La_2O_3 at 550 °C. Numbers, same as in previous figure.

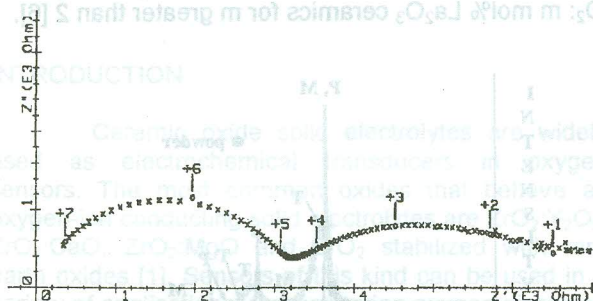


Fig. 4: Impedance diagram of ZrO_2 : 20 mol% La_2O_3 at 550 °C. Numbers, same as in previous figures.

These figures show that solid solution has been attained, at least partially. Otherwise, the dc resistivity would be larger than the values shown due to the electrical insulator character of ZrO_2 and of La_2O_3 at that temperature. The better resolution of a semicircle in the low frequency part of the impedance diagram in Fig.4, comparing with the impedance diagrams of Figs. 2 and 3, means that 20 mol% La_2O_3 is a quantity beyond its limit of solubility in ZrO_2 . In other words, La_2O_3 might be present in the grain boundary increasing then the grain boundary resistivity.

Fig. 5 shows the first attempt to study, by means of impedance spectroscopy, the tetragonal-to-

pyrochlore transformation known to occur in high temperature treated tetragonal zirconia-lanthania [6]. This is an Arrhenius plot of the resistance of a ZrO_2 : 15 mol % La_2O_3 sintered specimen. The resistance decreases as the temperature increases, as expected, but in the temperature range around 760 °C (T_s) - 920 °C (T_f) a change in the slope is observed, followed by the same previous trend for temperatures higher than 920 °C. A dilatometric analysis has been performed in

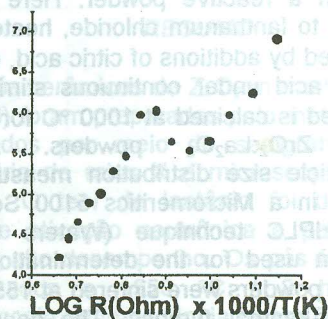


Fig. 5: Arrhenius plot of the bulk resistance of a ZrO_2 : 15 mol % La_2O_3 after *in situ* impedance spectroscopy measurements from 600 °C to 1250 °C.

cold-pressed specimens from the same powder batch to be sure that there is no modification in the geometric factor l/S (l and S are the sample thickness and electrode area, respectively) in that temperature range. The analysis indicates that a 1% linear retraction occurs at temperatures higher than 1200 °C, that could lead to a minor decrease in the resistivity above that temperature.

A differential thermal analysis has also been carried out in powders from the same batch that gave the results shown in Figs. 5 to look for phase transitions. The results are shown in Fig. 6.

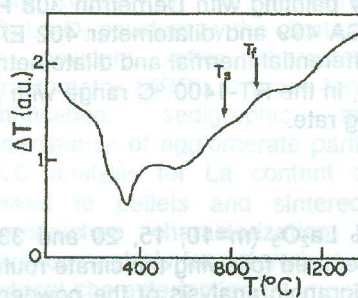


Fig.6: Differential thermal analysis of ZrO_2 :15 mol% La_2O_3 ceramic powders in the RT-1300 °C temperature range. T_s and T_f :refer to text for details.

As one can see, a transition occurs in the 800 °C - 950 °C. That transition is probably the tetragonal-

pyrochlore phase transition already studied by Bastide, Odier and Coutures [6]. Another experiment has been designed: powders from the same batch, that exhibit tetragonal phase, have been introduced to a furnace programmed to increase in temperature from RT to 1300 °C at 10 degrees/min. Samples have been withdrawn from the furnace when the temperature reached 1060 °C, 1160 °C, 1260 °C and 1400 °C. The results show that the pyrochlore phase is formed at the expenses of the tetragonal phase. Moreover, for the two higher temperatures, even diffraction lines due to the monoclinic phase are observed.

These results help explain the deviation in the Arrhenius plot shown in Fig. 5. The heating up of tetragonal $ZrO_2:La_2O_3$ specimens promotes the tetragonal-to-pyrochlore phase transformation, already reported [6]. That phase transformation, here detected at 840 °C in $ZrO_2: 15 \text{ mol\% } La_2O_3$, should increase the resistivity of the specimen if one takes into account that the tetragonal phase presents ionic conductivity higher than that of the monoclinic phase [7], and also higher than the pyrochlore phase, known to consist of an ordered array of anion (O^{2-}) vacancies. One assumes here that any ordering involving oxygen-ion vacancies should not contribute to the conductivity in zirconia ceramics.

CONCLUSIONS

Impedance spectroscopy measurements have been done in zirconia-lanthania ceramics prepared from powders obtained by the citrate chemical route in order to ascertain solid solution formation. It was shown that tetragonal-to-pyrochlore phase transitions in $ZrO_2:La_2O_3$ oxygen-ion conducting ceramics can be followed by *in situ* impedance spectroscopy. Electrical characterization of ionic conducting ceramic solid electrolytes by means of ac measurements can be correlated to structural phase transitions, provided the different phases have different ionic conductivities.

Acknowledgments: To FAPESP process number 92-2962/6 and to PADCT-Rare Earths/IQUSP for financial support. To Selma L. Silva, M. Durazzo and L. A. Genova, for X-ray, ATD and dilatometric measurements, respectively. To Dr. Noêmia M. P. de Moraes and Helena M. Shihomatsu for HPLC measurements. To Dr. E. N. S. Muccillo for helpful discussions and to Prof. M. Kleitz from LIESG, France, for kindly providing the IS software.

REFERENCES

- [1] DELL, R.M. and HOOPER, A. in: Solid Electrolytes, ed. HAGENMULLER, P. and VAN GOOL, W. (Academic Press, New York 1978) p.291.
- [2] Solid Electrolytes and their applications, ed. SUBBARAO, E. C., Plenum Press, New York, 1980.
- [3] YAMADA, K, SHINYA, Y. and TANAKA, K., Solid State Ionics 3/4 (1981) 595.

[4] ANDERSON, H. U., CHEN, C. C., WANG J. C. and PENNELL, M. J. in: Ceramic Powder Science III, Ceramic Transactions, Vol. 12, ed. MESSING, G. L., HIRANO, S. and HAUSNER, H. (The Am. Ceram. Soc., Westerville, Ohio, 1990) p. 749.

[5] PECHINI, M., U. S. Patent No. 3,330,697, July 11, 1967.

[6] BASTIDE, B, ODIER, P., COUTURES, J.P., J. Am. Ceram. Soc. 71, 6 (1988) 449-453.

[7] BUTLER, E. P., SLOTWINSKI, R. K., BONANOS, N., DRENNAN, J., STEELE, B. C. H. in Advances in Ceramics, Vol. 12, Science and Technology of Zirconia II, Eds.: CLAUSSEN, N., RÜHLE, M., HEUER, A. H. The Am. Ceram. Soc., USA (1984) p. 572-584.