Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 35 (2009) 467–470
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

High-temperature electrical properties of lanthanum beta-alumina solid electrolytes

G.C.C. Costa, R. Muccillo *

Center of Science and Technology of Materials, Energy and Nuclear Research Institute, CP 11049, S. Paulo 05422-970, SP, Brazil

Received 1 October 2007; received in revised form 25 December 2007; accepted 2 January 2008
Available online 8 April 2008

Abstract

Impedance spectroscopy measurements were carried out in the 10 Hz to 10 MHz frequency range from 500 to 1200 °C in $LaAl_{11}O_{18}$ pellets sintered at 1600 °C. The powders were obtained by the polymeric precursor technique. The sintered pellets were nearly single phase $LaAl_{11}O_{18}$. The bulk electrical resistivity was evaluated from the $[-Z''(\omega) \times Z'(\omega)]$ impedance diagrams. The value of the activation energy for the ionic conduction, 0.89 eV, was determined from the Arrhenius plot of the bulk conductivity. An yttria-stabilized zirconia (YSZ) oxygen pump and an YSZ oxygen sensor were used for providing 10–1500 ppm of partial pressure of oxygen (pO_2) at 1000 °C for determining the electromotive force (emf) in a Pt/$LaAl_{11}O_{18}$/Cr_2O_3 + Cr electrochemical cell. The results follow the Nernst law. The high signal-to-noise ratio of the emf at low pO_2 values shows that the $LaAl_{11}O_{18}$ specimens may be used in sensors for detection of oxygen at high temperatures.

Keywords: C. Ionic conductivity; D. β-Al_2O_3; E. sensors

1. Introduction

Oxygen sensors based on the oxygen ion conducting stabilized zirconia solid electrolytes operating in the potentiometric mode have been used in the analysis and control of oxygen in a wide variety of situations [1]. The voltage across the solid electrolyte is proportional to the logarithm of the concentration of mobile species according to the Nernst equation, the sensors being called Nernstian sensors. The applications are mainly in two situations: (1) for monitoring oxygen in the exhaust gas of combustion engine vehicles to control the air–fuel ratio at levels close to stoichiometry to minimize emission of pollutants and (2) in harsh chemical environment at high temperatures during processing of molten steel. In steelmaking processes, control of oxygen levels in the molten steel is essential and this control is usually done with electrochemical oxygen probes. These probes consist of a solid electrolyte and a reference electrode and several components like thermocouple, refractory case, and metallic terminal leads for measuring the electromotive forces resulting from the solid electrolyte and the thermocouple. The electrochemical sensors are not limited to detecting the species that is mobile in the electrolyte because the equilibrium between an immobile species and mobile species establishes a concentration of the mobile species, which can generate an electromotive force that is related to the concentration of the immobile species [2]. Nernst oxygen sensors based on partially stabilized zirconia solid electrolytes, which are oxide ion conductors, are not suitable for measuring high concentrations of oxygen in a potentiometric mode due to their logarithm dependence on the oxygen level [3].

The measurement of oxygen in molten metals has already been achieved using a variety of beta aluminas [4,5] based on the fact that it is not required that the element to be sensed is the mobile ion in the electrolyte. Ion exchange at the surface of the electrolyte can occur and the element can be sensed [5]. Nernstian oxygen sensors based on a strontium, calcium or lanthanum ion conducting electrolyte with a beta-alumina type structure have been developed [5,6]. These sensors respond to lower oxygen contents than the conventional oxygen sensors based on stabilized zirconia.

In this paper the electrical behavior of $LaAl_{11}O_{18}$ (La–β-Al_2O_3) solid electrolytes is described. Emphasis is done on the evaluation of the emf response of nearly single phase

* Corresponding author. Tel.: +55 11 31339203; fax: +55 11 31339203.
E-mail address: muccillo@usp.br (R. Muccillo).

0272-8842/$34.00
doi:10.1016/j.ceramint.2008.01.004

$LaAl_{11}O_{18}$ compounds, using powders synthesized by the polymeric precursor technique.

2. Experimental

Details of the chemical synthesis of $LaAl_{11}O_{18}$ powders by the polymeric precursor technique have recently been described [7]. Briefly, stoichiometric amounts of lanthanum nitrate and aluminum nitrate were added to citric acid and ethylene glycol and heated under stirring to produce a polymeric resin. Calcination of the resin yielded high surface area powders. The powders were processed before sintering in an attritor mill with yttria-stabilized zirconia (Tosoh 3Y, Japan) spheres as milling media.

The powders were pressed uniaxially (100 MPa) and isostatically (200 MPa) into cylinders (10 mm diameter × 1 mm thickness) and sintered in air at 1600 °C for 2 h with 10 °C/min heating and cooling rates. Phase composition evaluated by X-ray diffraction shows that these specimens are nearly single phase [7].

For electrical measurements, platinum paste was applied to the parallel surfaces of the sintered specimens and cured at 800 °C. The electrical properties were studied by impedance spectroscopy in the 500–1200 °C range with a Hewlett–Packard 4192A LF impedance analyzer connected to a HP 362 controller. An alumina sample holder, with an S-type thermocouple with its junction close to the specimen, and platinum leads, was used inside a Lindberg-BlueM tubular furnace. The $[-Z''(\omega) \times Z'(\omega)]$ impedance spectroscopy data were collected in the 10 Hz to 10 MHz frequency range. A special software was used for collecting and analyzing the impedance spectroscopy data [8].

For the study of the dependence of the electromotive force generated in the $LaAl_{11}O_{18}$ solid electrolyte, an experimental setup consisting of an yttria-stabilized zirconia (YSZ) oxygen pump and an YSZ oxygen sensor was mounted, Fig. 1 [9]. The vector gas with a known amount of oxygen is fluxed inside a furnace where the solid electrolyte is inserted. The solid electrolyte was prepared in the form of a one-end closed tube by cold-pressing, pre-sintering at 1000 °C, drilling in a lathe, and sintering at 1600 °C. The oxygen reacts with the external part of the tube while in the internal part a Cr_2O_3–Cr reference establishes a known pO_2. The internal and the external parts of the solid electrolyte are made airtight using quartz tubes and high-temperature cement. Details of the solid electrolyte are also shown in the bottom of Fig. 1. The electrochemical probe consisted of a half-cell $Cr + Cr_2O_3/LaAl_{11}O_{18}$ with platinum lead wire.

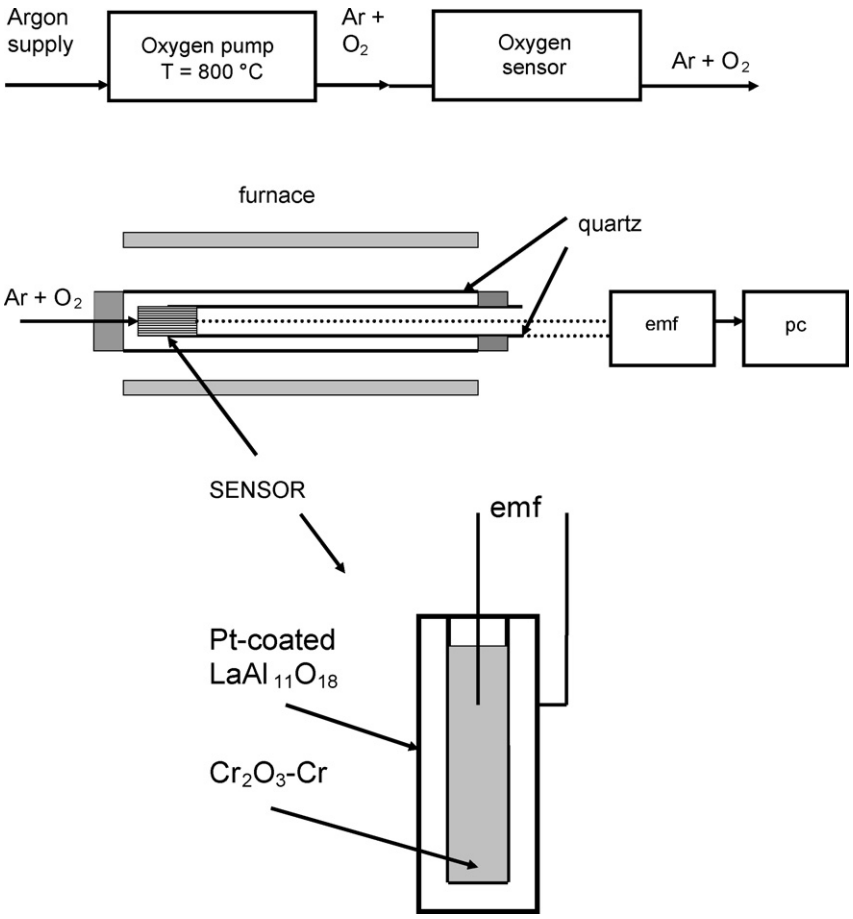

Fig. 1. Scheme of the experimental setup for determining the electrical response of the $LaAl_{11}O_{18}$ to the partial pressure of oxygen; in the bottom a detail of the one-end closed tubular ceramic sensor is shown.

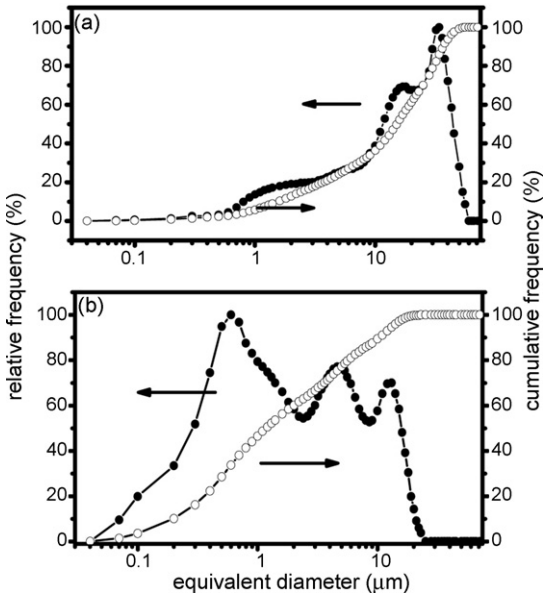

Fig. 2. Distribution of particle size of La–β-Al_2O_3 powders synthesized by the polymeric precursor technique before (a) and after (b) attrition milling.

3. Results and discussion

Fig. 2 shows the particle size distribution of $LaAl_{11}O_{18}$ powders before and after attrition milling. The attrition milling was carried out for breaking agglomerates and to improve the density of the sintered pellets. The distributions of average powder diameter before milling is determined with 90% of the particles with an average <36.7 μm, 50% < 15.5 μm and 10% < 1.5 μm. After 1 h attrition milling (1 mm diameter Tosoh YSZ spheres in isopropanol, 1200 rpm) the particle size distribution (Fig. 2b) shows 90% < 10.3 μm, 50% < 1.2 μm and 10% < 0.2 μm. A shift to the left (smaller average particle size) in Fig. 2b is observed. Transmission electron microscopy analysis showed that the particles are indeed composed of hard agglomerates [7] and that attrition milling the La–β-alumina powders helps sintering the powder compacts.

Fig. 3 shows impedance spectroscopy diagrams of $LaAl_{11}O_{18}$ pellets sintered at 1600 °C for 2 h. These diagrams were measured at 1000, 1100 and 1200 °C in the 1 kHz to 10 MHz frequency range. One well-resolved semicircle is measured at high frequencies, intercepting the origin, associated with intragranular or bulk electrical properties of the electrolyte [10,11]. This is confirmed by the determination of the bulk capacitance $C_b = 1/(2\pi f_{0b} R_b)$. The value of f_{0b} is determined at the apex of the semicircle, and the value of R_b at the intersection of the semicircle with the Z' axis. The capacitance value determined in the impedance diagram may be used to help in the identification of the nature of a relaxation process [12,13]. The capacitance is in the 10^{-11} to 10^{-12} F/cm range, corresponding to bulk capacitances. In the low frequency region of the impedance diagram a few points reveal the presence of another semicircle probably due to blocking of charge carriers at grain boundaries [10]. An estimate of the associate capacitance due to grain boundaries C_{gb} gives $\sim 6 \times 10^{-8}$ F/cm, typical of grain boundary capacitances [12,13].

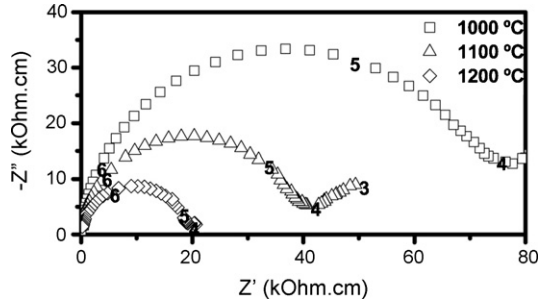

Fig. 3. Impedance spectroscopy diagrams of La–β-Al_2O_3 pellets sintered at 1600 °C for 2 h; pellets prepared with powders synthesized by the polymeric precursor technique.

The Arrhenius plot of the bulk conductivity of a $LaAl_{11}O_{18}$ sintered pellet is shown in Fig. 4. In the 500–900 °C range an activation energy of 0.89 eV is determined, in agreement with previous results for Sr–Li–β-alumina (0.86 eV) and for Sr–Mg–β″-alumina (0.9 eV) [14]. Another feature of the Arrhenius plot shown in Fig. 4 is a deviation of the straight line for temperatures higher than 900 °C. High-temperature *in situ* X-ray diffraction in that range did not show any evidence of structural phase transition [15]. Further experimental work is required for a better understanding of the high-temperature Arrhenius behavior of $LaAl_{11}O_{18}$ solid electrolytes.

The possibility of using $LaAl_{11}O_{18}$ sintered pellets in devices for measuring oxygen levels at high temperatures was analyzed. An experimental setup consisting of (one-end closed) tubes of sintered $LaAl_{11}O_{18}$ with Pt electrodes and Cr_2O_3 reference electrode was positioned inside a tubular furnace. The reservoir containing the solid electrolyte tube was connected to a "pO_2 station" for providing controlled amounts of O_2 in the 10 ppm–1 atm range. Fig. 5 shows the electrical response at 1000 °C for continuous insertion of oxygen at different levels, turning on and off at 10 min intervals. This temperature of

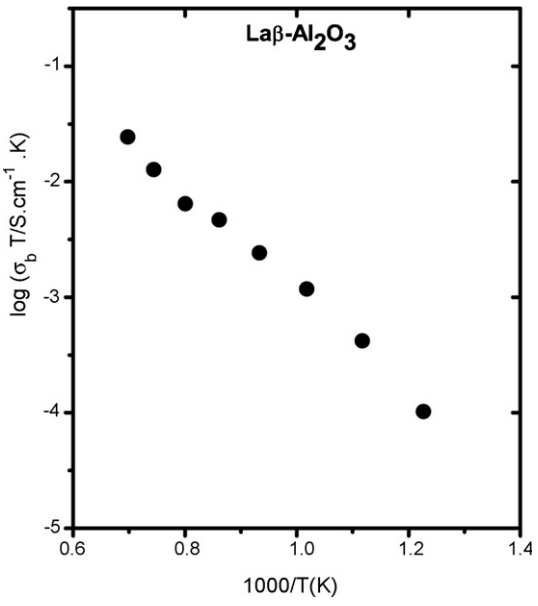

Fig. 4. Arrhenius plot of the bulk conductivity of a $LaAl_{11}O_{18}$ solid electrolyte pellet sintered at 1600 °C for 2 h.

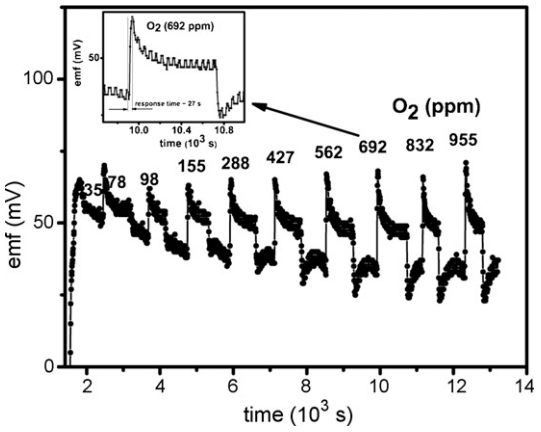

Fig. 5. Electrical response of the $LaAl_{11}O_{18}$ solid electrolyte at 1000 °C for increasing amounts of oxygen. (Inset) Shape of the dc electrical response of $LaAl_{11}O_{18}$ at 1000 °C for 692 ppm oxygen.

measurement was chosen because it was found it is the minimum temperature that provides stationary emf values, i.e., the $LaAl_{11}O_{18}$ solid electrolyte starts showing an oxygen sensing behavior at this temperature. The inset of Fig. 5 shows details of the fem response as a function of exposure time. After exposure of the solid electrolyte to oxygen, the emf reaches a maximum value in approximately 27 s, which is the response time of the $LaAl_{11}O_{18}$ solid electrolyte at 1000 °C. This may be considered a reasonable value. The response time of commercial zirconia–magnesia solid electrolytes for insertion in molten steels, for temperatures much higher, 1500–1600 °C, is in the 6–10 s range [16,17].

A detailed analysis of the dependence of the amplitude of the emf signal on the oxygen content was carried out. Fixed amounts of oxygen gas were inserted in the carrier gas, argon, and introduced to the $LaAl_{11}O_{18}$ sensor at 1000 °C. When the equilibrium is reached it is expected the Nernst law is obeyed: $E = [RT/4F]\ \ln[p^{I}/p^{II}]$, where E is the electromotive force, R the universal gas constant, F the Faraday constant, and p^{I} and p^{II} the partial pressures of oxygen to be measured and of the reference, respectively. Fig. 6 shows the dependence of emf on the partial pressure of oxygen at 1000 °C. A good correlation is found showing that $LaAl_{11}O_{18}$ can be used as a Nernstian potentiometric sensor.

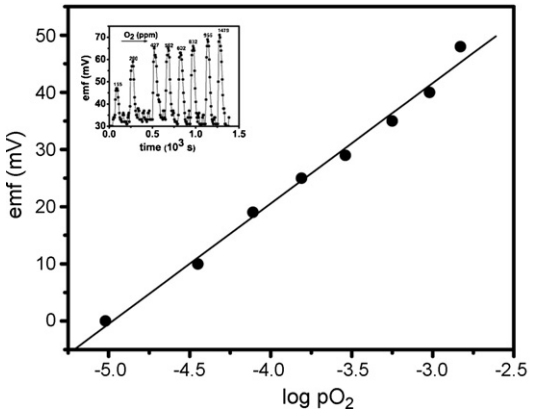

Fig. 6. Dependence of the electromotive force of $LaAl_{11}O_{18}$ on the partial pressure of oxygen at 1000 °C.

4. Conclusions

Impedance spectroscopy diagrams were measured in nearly single phase $LaAl_{11}O_{18}$ pellets obtained after sintering at 1600 °C powders prepared by the polymeric precursor technique. The diagrams in the 500–1200 °C show bulk and grain boundary contributions to the electrical resistivity. The bulk activation energy for electrical conduction was determined as 0.89 eV for sintered specimens. A Nernstian behavior was found for specimens exposed to oxygen in the 100–1500 ppm range at 1000 °C, indicating they can be used for high-temperature detection of oxygen.

Acknowledgements

To CNEN, CNPq (Proc. 306496/88-7) and FAPESP (Procs. 05/53241-9 and 98/14324-0) for financial support. One of the authors (GCCC) acknowledges CAPES for the M.Sc. scholarship.

References

[1] K.P. Jagannathan, S.K. Tiku, H.S. Ray, A. Ghosh, E.C. Subbarao, Technological applications of solid electrolytes, in: E.C. Subbarao (Ed.), Solid Electrolytes and their Applications, Plenum Press, New York, 1980, pp. 201–259.
[2] J.W. Fergus, Using chemical sensors to control molten metal processing, J. Met. 52 (10) (2000) 1–14. http://www.tms.org/pubs/journals/JOM/0010/Fergus/Fergus-0010.html.
[3] R.W. Gibson, R.V. Kumar, D.J. Fray, Novel sensors for monitoring high oxygen concentrations, Solid State Ionics 121 (1–4) (1999) 43–50.
[4] A. Davies, D.J. Fray, S.R. Witek, Measurement of oxygen in steel using beta-alumina electrolytes, Ironmaking and Steelmaking 22 (4) (1995) 310–315.
[5] D.J. Fray, The use of solid electrolytes as sensors for applications in molten metals, Solid State Ionics 86–88 (1996) 1045–1054.
[6] R.V. Kumar, D.J. Fray, Application of novel sensors in the measurement of very low oxygen potentials, Solid State Ionics 70 (1994) 588–594.
[7] G.C.C. Costa, R. Muccillo, Synthesis of lanthanum beta-alumina powders by the polymeric precursor technique, Ceramics International, in press.
[8] M. Kleitz, J.H. Kennedy, in: P. Vashishta, J.N. Mundy, G.K. Shenoy (Eds.), Fast Ion Transport in Solids, Elsevier/North-Holland, The Netherlands, 1979, p. 185.
[9] M.C. Steil, F.C. Fonseca, Y.V. França, J.F.Q. Rey, E.N.S. Muccillo, R. Muccillo, An experimental setup for electrical measurements as a function of temperature and partial pressure of oxygen, Ceramica 48 (307) (2002) 146–152. www.scielo.br/pdf/ce/v48n307/13831.pdf.
[10] M. Kleitz, H. Bernard, E. Fernandez, E. Schouler, Science and technology of zirconia, in: A.H. Heuer, L.W. Hobbs (Eds.), Advances in Ceramics, 3, The Am. Ceram. Soc., Columbus, OH, 1983, p. 310.
[11] J.R. Macdonald, W.B. Johnson, in: J.R. Macdonald (Ed.), Impedance Spectroscopy—Emphasizing Solid Materials and Systems, John Wiley & Sons Inc., N. York, 1987.
[12] J.T.S. Irvine, D.C. Sinclair, A.R. West, Advanced Materials 2 (1990) 132–138.
[13] J.G. Fletcher, A.R. West, J.T.S. Irvine, The ac impedance response of the physical interface between yttria-stabilized zirconia and $YBa_2Cu_3O_{7-x}$, Journal of the Electrochemical Society 142 (8) (1995) 2650–2654.
[14] G.W. Schaefer, W. Weppner, Preparation of divalent beta-alumina ceramics via ion-exchange from κ-alumina and Na–beta-alumina ceramics, Solid State Ionics 53–56 (1992) 559–563.
[15] G.C.C. Costa, M.Sc. Dissertation, University of S. Paulo, Brazil, 2006.
[16] K. Yamada, T. Shinya, K. Tanaka, Properties of oxygen sensors for steelmaking, Solid State Ionics 3–4 (1981) 595–598.
[17] Q. Liu, S. An, W. Qiu, Study on thermal expansion and thermal shock resistance of Mg–PSZ, Solid State Ionics 121 (1–4) (1999) 61–65.