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Electrochemical characterization of nanostructured zirconias

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ABSTRACT

Redox stability of cubic nanostructured zirconia ceramics, free of any secondary phases, has been investigated experimentally as a function of grain size. Pure 8 mol% Y_2O_3-doped ZrO_2 powders were synthesized by a spray pyrolysis process and then compacted by uniaxial pressing, followed by cold isostatic pressing. Using appropriate thermal treatments, average grain sizes ranging from 25 to 242 nm and relative densities from 71% up to 98% were obtained. An electrochemical characterization was performed with comparison on ceramics of 3.2 and 7.6 µm and 98% of theoretical density starting from commercial YSZ powder.

1. Introduction

Yttria stabilized zirconia (YSZ) is the most commonly used solid electrolyte for high temperature SOFCs because of its good electrical conductivity and high ionic transport number in both oxidizing and reducing atmospheres from 850 to 1000 °C. The development of oxygen conducting solid electrolytes at temperatures lower than 800 °C is of great importance for large-scale development of applications, such as “intermediate temperature” solid oxide fuel cells (IT-SOFCs), or electrocatalytic reactors for natural gas conversion. None of the alternative electrolytes proposed fulfills the requirements in terms of stability, or electronic transport number in reducing atmospheres.

Decreasing membrane thickness is also an alternative in order to decrease the ohmic loss at low temperatures but only to a certain extent. An ideal electrolyte is expected to present sufficient mechanical strength, no pores or cracks, which is difficult for a thin film. Moreover, it has been shown that on reducing the membrane thickness, a transition can occur from an overall process predominantly controlled by diffusion through the electrolyte, to a surface exchange limiting process [1–3]. Consequently, for given experimental conditions, no appreciable gain can be obtained by fabricating thinner membranes below a characteristic value, L_c. Guillodo et al. [4] have reported L_c values for various solid electrolytes.

Another approach concerns the control of the oxide electrolyte microstructure. The role of the microstructure, such as grain size, grain boundaries, pores and second phases, on the electrolyte conductivity has been much debated in recent years. Large discrepancies between the published results are observed [5–8]. It should be pointed out that the key difference between the published results is the manner in which the nanocrystalline samples were prepared as bulk or thin films, since the blocking effect appears to be mainly controlled by the density of the grain boundaries. It is expected that nanostructured materials (i.e. materials with grain sizes (d_g) less than 100 nm) exhibit a higher grain boundary conductivity than that of microcrystalline samples due to a dominant interfacial area and size-dependent defects [9]. Indeed, an enhancement of about 2 orders of magnitude was measured (i) by Mondal et al. [5] in nearly pure tetragonal zirconia ceramics with d_g of 25–50 nm, (ii) by Kosacki [11] in 8YSZ thin films with d_g of 20 nm. From Boulfrad et al. [8], the grain boundaries were found to be intrinsically resistive even for nanostructured ceramics with d_g less than 100 nm. Although the specific resistivity of the blocking contribution decreases with decreasing grain size, it remains about 100 times higher than the bulk resistivity. Without any impurity phases, the cause of this "intrinsic" blocking effect is still unclear. Many authors have studied the intra-grain (bulk) and grain boundary contributions to the total conductivity and especially the role of the space charge contribution within the grain boundaries [9,10]. Reduction in grain size has also a considerable effect on the stabilization of tetragonal zirconia from a thermodynamic point of view [11,12] and on an enhancement of mechanical properties such as the wear resistance [13].

The domain of electrochemical stability where zirconia can be used in galvanostatic cells is limited by the onset of a chemical reduction of the material. Severe electrochemical reductions of stabilized zirconias due to the passage of high current densities were investigated in the early 60’s in connection with the application as MHD (Magnetohydrodynamics) electrodes [14]. Such a reduction phenomenon has been observed during various processes, such as: wetting of zirconias with molten metals [15], monitoring of the oxygen stoichiometry of oxides using electrochemical

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cells [16], and oxygen partial pressure control and monitoring (oxygen pump or oxygen trap). Numerous techniques have been used for the identification of blackened zirconias [17], i.e., optical spectroscopy, E.P.R., electron microscopy, X-ray diffraction, dielectric measurement, mechanical property studies, or electrical conductivity. In the seventies, Fabry et al. [18] carried out original electrochemical studies after controlled galvanostatic or potentiometric reduction processes of stabilized zirconias. More recently, Janek [17] has studied the electrochemical reduction on both polycrystals of calcia-stabilized zirconia and single crystals of yttria-stabilized zirconia at 500 °C. Although various reaction schemes have been proposed, the nature of the defects responsible of zirconia blackening is still under discussion. The purpose of this paper is to evaluate the role of the grain size on the reducibility of stabilized zirconia.

2. Basic principles

In the case of an electrolyte conducting purely by oxide ions, the role of a dc current through an electrode can be described within the "microsystem" concept [19]. The electrode formed by the contact between a metal, a solid oxide electrolyte and a gas is viewed as measuring the oxygen activity in the microsystem that exchanges oxygen from the surrounding gas more or less easily. The local balance of oxygen in the microsystem takes into account the fluxes of adsorption (J_{ads}) and desorption (J_{des}) of oxygen and the flux corresponding to the electrode reaction (J_{ER}), i.e., either an uptake or release of oxygen, according to:

$$\frac{1}{2}O_2 + 2e^- \Leftrightarrow O^{2-} \tag{1}$$

Under steady state, the balance of the fluxes can be written:

$$J_{ads} \pm J_{ER} = J_{des} \tag{2}$$

On the cathode side of the cell, the gas fixes the maximum adsorption flux; this flux corresponds to a limiting cathodic current (I_{lim}) for which the oxygen activity in the microsystem is nil. For a current higher than I_{lim}, a direct injection of electrons within the solid electrolyte will occur simultaneously with the oxygen reaction (1). In galvanostatic conditions, two situations are encountered:

- If the cathodic dc current is lower than $|I_{lim}|$. The mass balance within a layer of the solid electrolyte near the cathode indicates that no stoichiometry change is obtained; only an oxide ions flux from the cathode to the anode is observed: this flux J obeys Faraday's law, i.e., $J = I/2F$. The cell works as an oxygen pump.
- If the applied cathodic current I is higher than $|I_{lim}|$, the current obeys the following equation:

$$I = I_{lim} + I_e \tag{3}$$

The current I_e corresponds to injection of electrons that are trapped on the point defects. As shown in Fig. 1, the mass balance of oxide ions in a layer near the cathode of the cell demonstrates that the oxide becomes non-stoichiometric. It could be easily demonstrated that this non-stoichiometric zone progresses within the oxide from the cathode to the anode [18,20].

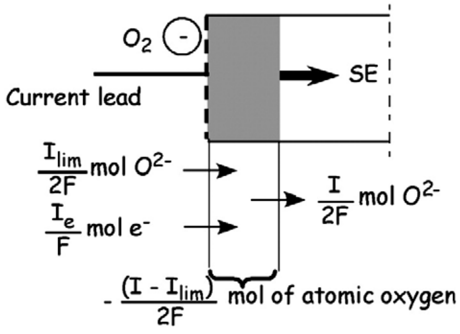

Fig. 1. Schematic representation of the cathode processes on an oxide electrolyte: electrochemical reduction of the oxide electrolyte.

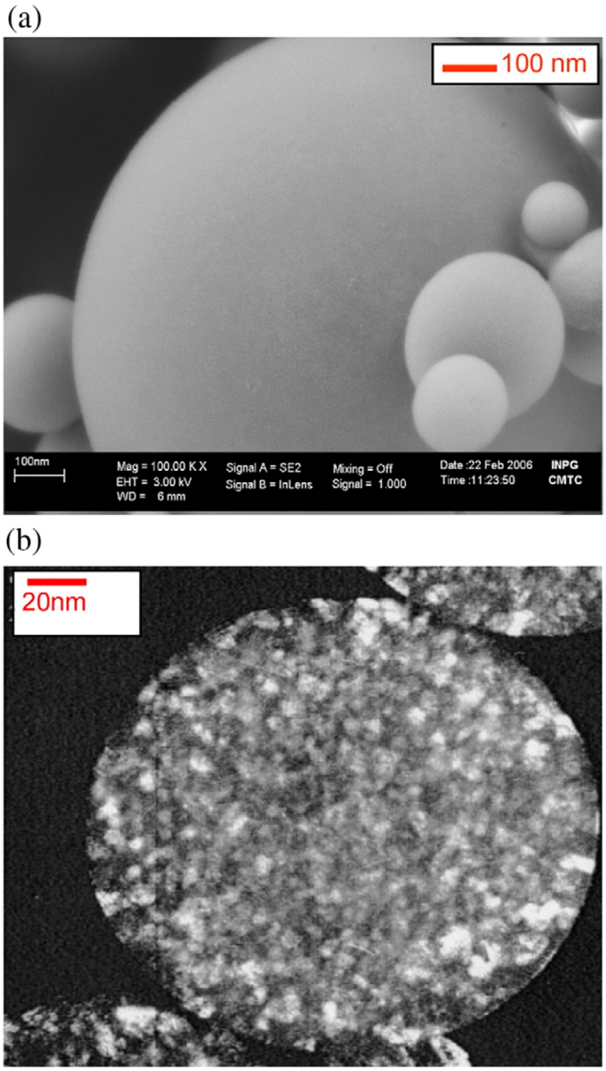

Fig. 2. (a) FEG-SEM micrography of the 8YSZ powder obtained by spray pyrolysis, (b) TEM observation of the 8YSZ powder (dark field image).

Basically, a partial reduction of a solid electrolyte is related to a valence change either of the basic cation (Zr^{4+} in the case of zirconia) or of a point defect (a dissolved chemical impurity or a structural defect such as an oxide-ion vacancy).

The main features associated with electrochemical reduction are [21]: (i) a variation of the stoichiometry ratio due to oxygen release, (ii) a variation of the ionic and electronic conductivities, (iii) a coloration due to trapped electrons which can be excited to higher energy levels, (iv) a variation of the electrode potential which varies as a function of the reduction degree.

3. Experimental

3.1. Preparation of zirconia samples

The 8 mol% yttria stabilized zirconia (referred to as 8YSZ) samples were prepared from powders obtained by spray pyrolysis using an ultrasonic atomizer (ultrasonic frequency: 1.7 MHz) [22,23]. The precursors solutions were made with a stoichiometric mixture of hexahydrate zirconyl nitrate $ZrO(NO_3)_2{\cdot}6\ H_2O$ (Aldrich, 99%) and