

Preparation and Characterization of YSZ Closed-End Tubes for Oxygen Sensors

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Abstract. Closed-end tubes of yttria-stabilized zirconia (YSZ) are required in oxygen sensors for automotive applications to control fuel consumption and pollutant emission. High temperature oxygen sensors were prepared by electrophoretic deposition (EPD) of submicron YSZ particles after suitably adjusting the rheological characteristics of the suspension of the ceramic particles in alcoholic medium. The ceramic tubes were analyzed by X-ray diffraction and impedance spectroscopy. The morphology of sintered specimens was studied by scanning electron microscopy. The processing by EPD of tubular ceramic solid electrolytes with electrical conductivity similar to the ones found in commercial lambda sensors has been successfully achieved.

Introduction

Zirconia stabilized with 8 mol% yttria (8YSZ) is a ceramic material largely used as solid electrolyte in oxygen sensors [1,2] and in solid oxide fuel cells [3] due to its high oxide ion conductivity at temperatures higher than approximately 400 °C, the onset of the electrolytic domain and thermal stability.

The solid electrolyte configuration in commercially available oxygen sensors is closed-end tube specimens for large contact area with the measuring medium. Several methods can be used to fabricated tubular specimens [4,5]. The electrophoretic deposition (EPD) is a suitable technique for manufacturing ceramic pieces with complex geometry shapes [6]. The deposition is achieved by applying a dc electric field on a metallic substrate immersed into a suspension containing the ceramic particles. The control of the shape is possible through electrode design and knowledge of the shrinkage behavior of the ceramic piece upon sintering. The mechanism of EPD has two main steps [6-8]: first, a dc electric field is applied to a suspension of the ceramic particles forcing these charged particles to move towards an oppositely charged electrode; second, the particles are deposited onto the electrode producing a relatively dense and homogeneous compact or film.

A fundamental requirement for a successful application of the EPD technique is the production of a stable suspension of particles in a suitable solvent and with a high zeta potential, i.e., with charged particles. The incorporation of charge on the surface of the particles is achieved by ion adsorption or by creating an electric double layer. The electric double layer provides the stabilization of the particles in the suspension and allows the motion of the particles under an electric field [9].

In the present work, ceramic suspensions were prepared with $ZrO_2:8 \text{ mol\% } Y_2O_3$ with a bimodal distribution of particle size. The reactivity of the ceramic powder dispersed in alcoholic medium with the addition of dispersant was monitored. The main idea was to establish suitable conditions for preparing stable suspensions for obtaining simultaneously several closed-end tubes without cracks after burning out the substrate (graphite rod), drying the green ceramic tube in different atmospheres and sintering to high density to obtain ceramic pieces impervious to oxygen.

Experimental

The 8YSZ was a commercial powder from Tosoh, USA (TZ-8Y granules of specific surface area $16 \pm 3 \text{ m}^2/\text{g}$). Part of the 8YSZ powders was calcined at 850°C for 1 h for producing the larger size granules ($19.5 \text{ }\mu\text{m}$ average granule size).

A mixture of 70 wt.% as-received 8YSZ ($0.75 \text{ }\mu\text{m}$ size granules) and 30 wt.% 8YSZ ($19.5 \text{ }\mu\text{m}$) was dispersed in isopropanol (1 vol.% of solids) under ultrasound for 30 min to break up agglomerates as well as for homogenization. The stability of the suspension was monitored by evaluating the electrophoretic mobility (ESA 9800 Matec Applied Sciences) as a function of dispersant concentration (4-hydroxybenzoic acid). The dispersant/solvent volume ratio was 5g/100 mL.

The ceramic particles in suspension were electrophoretically deposited into a cylindrical graphite under 80 V (HP 6116A power supply) for 2 min. The tubes were dried in air and in KCl environment, and fired at 900°C for 2 h for burning out the graphite, and sintered at 1500°C for 0.5 h.

The sintered tubes were cross-sectioned and 2 mm thickness rings were analyzed. The apparent density was evaluated by the Archimedes method, the structural phases by X-ray diffraction (Bruker-AXS model D8 Advance, Cu- k_α radiation, 40 kV-40 mA), and the electrical conductivity by impedance spectroscopy at 400°C (HP 4192A impedance analyzer). The ceramic morphology of the fractured surfaces was observed by scanning electron microscopy (Quanta model 600 FEG).

Results and discussion

Fig. 1 shows the dependence of the electrophoretic mobility of the 8YSZ ceramic granules in isopropanol on the content of 4-hydroxybenzoic acid dispersant. The measured value for the 8YSZ granules at pH 6.9 in isopropanol without dispersant is $0.265 \times 10^{-8} \text{ m}^2/\text{Vs}$. This spontaneous charging of the mobile species and the pH value for suspension may be explained by the low amount of H_2O in the solvent [10]. Fig. 1 shows that H^+ ions are adsorbed at the surface of the ceramic powder. The electrophoretic mobility depends on the H^+ adsorption in the alcoholic medium. The concentration of ions and their behavior at the granule surfaces depend on the alcoholic medium used in the suspension. The addition of 4-hydroxybenzoic acid as dispersant (~ 0.25 -4 wt.%) improved the electrophoretic mobility of the 8YSZ particles in isopropanol medium.

Taking into account the electrophoretic mobility results, ceramic suspensions were prepared using 3 wt.% of the dispersant for testing the deposition of the 8YSZ. Fig. 2 shows the pieces after drying in KCl (left) and after burning out the graphite and densification (right).

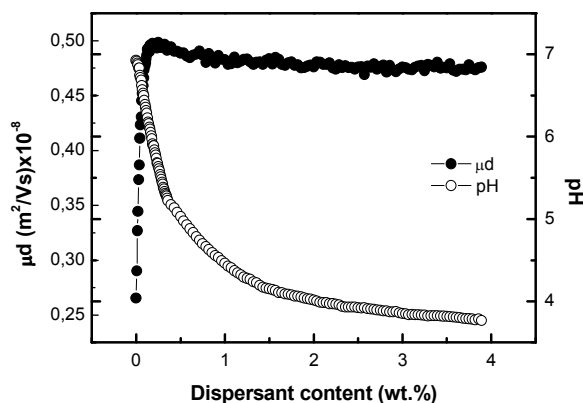


Fig. 1. Dependence of the electrophoretic mobility of 8YSZ particles on the dispersant content.

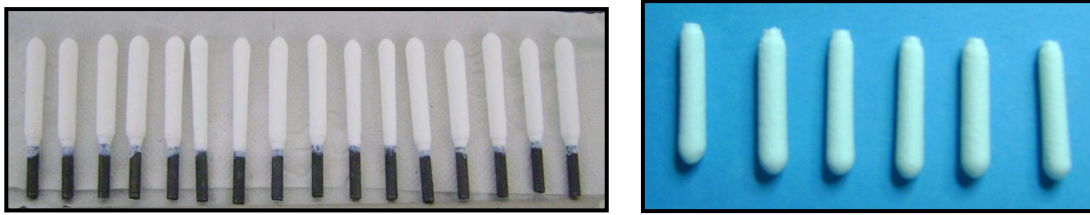


Fig. 2. Left: 8YSZ one-end closed tubes deposited by electrophoresis onto graphite electrodes, after drying in KCl. Right: 8YSZ after sintering at 1500 °C .

Fig. 3 shows results of X-ray diffraction measurements of the sintered 8 mol% yttria-stabilized zirconia tubes prepared by EPD, after drying in air and KCl. The patterns are of a cubic phase. The apparent density is higher than 92%TD. The achieved densification shows that the sintered tubes are impervious to oxygen and therefore may be used in oxygen sensors.

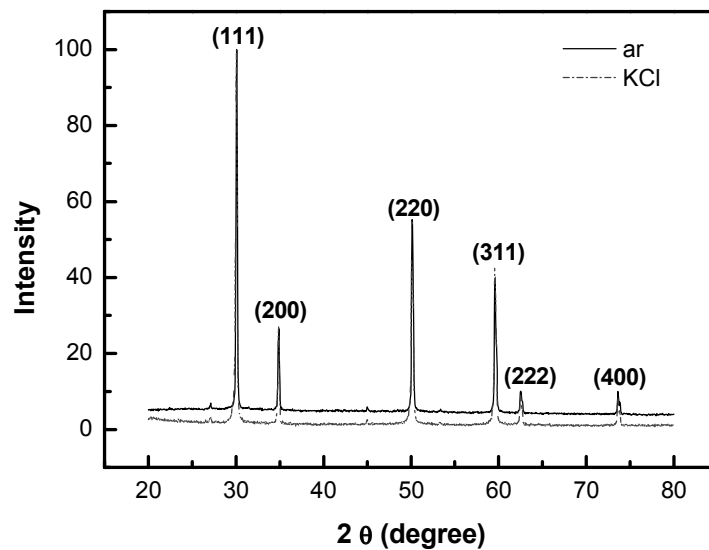


Fig. 3. X-ray diffraction patterns of 8 mol% yttria-stabilized zirconia solid electrolyte obtained by EPD.

Fig. 4 shows micrographs of fracture surfaces of the sintered 8YSZ ceramic tube prepared by EPD. Changing the drying medium does not change the morphological aspects of the fractured surfaces. The fractures are mainly transgranular with two main distinct regions: dense (dark) and porous. Cracks are probably caused by fracturing during the preparation of the specimen for observation.

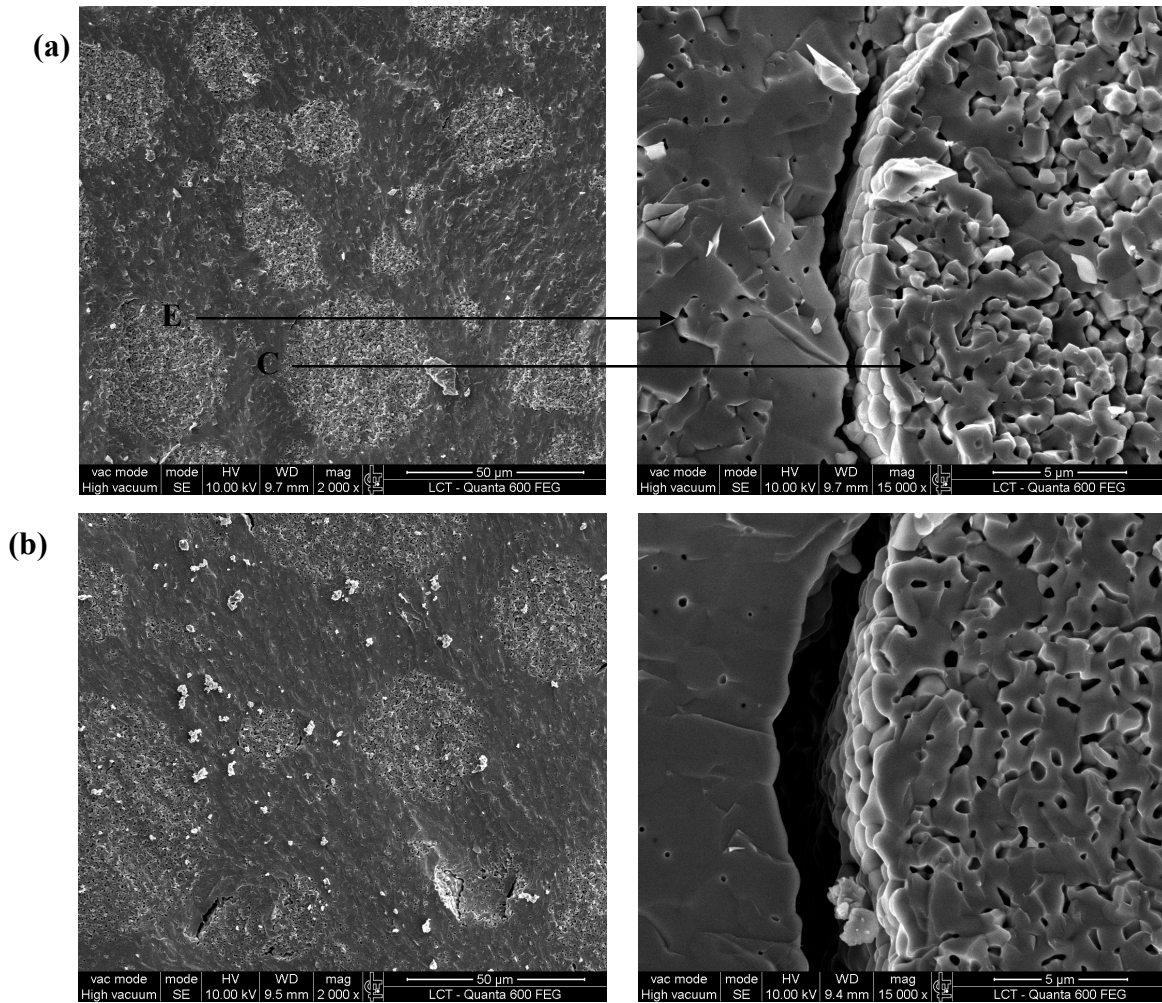


Fig. 4. Scanning electron microscopy micrographs of the fracture surface of the sintered 8YSZ tube prepared by electrophoretic deposition after drying in air (a) and in KCl (b).

The impedance spectroscopy diagrams of the samples, evaluated at 400°C, are shown in Fig. 5. There are two components, one at high frequencies, due to intragranular resistivity, and another at low frequencies (grain boundary resistivity) [11]. The total electrical resistivity is of the same order of magnitude of values measured in YSZ sensors at that temperature.

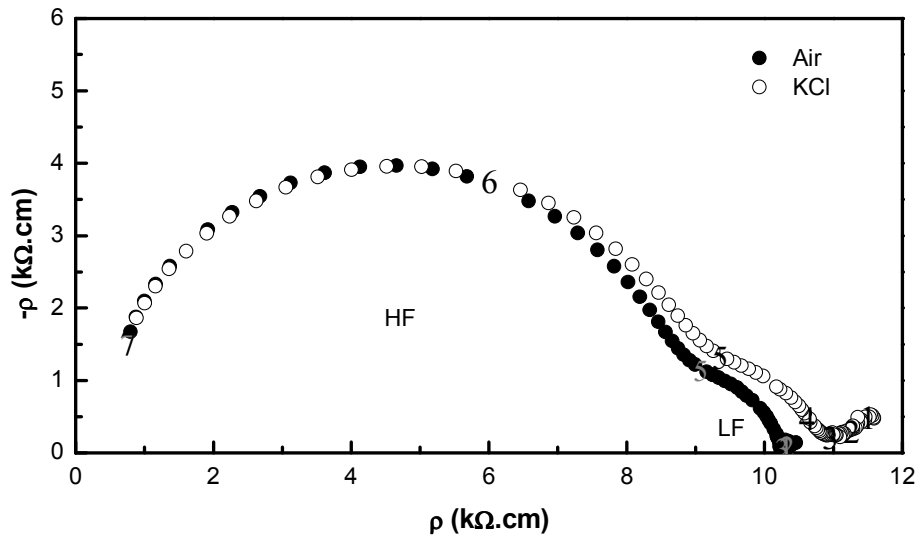


Fig. 5. Impedance spectroscopy diagrams, measured at 400 °C, of the sintered 8YSZ electrolyte electrophoretically deposited. The numbers stand for the logarithm of the frequency (Hz).

Summary

Yttria-stabilized zirconia closed-end tubes have been successfully prepared by electrophoretic deposition. The conditions for depositions of thin layers of ceramic particles for producing impervious to oxygen ceramic tubes have been determined.

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