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Spray-Dried YSZ Ceramic Powders: Influence of Slurry Stability on Physical Characteristics of Agglomerates

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Abstract. Zirconia stabilized with 8 mol% yttria (YSZ) is the most effective material for use as electrolytes in solid oxide fuel cell. Ceramic powders of YSZ were synthesized in IPEN by coprecipitation route and are composed by fine particles (less than 01μm) with large surface area (~60$m^2.g^{-1}$). These powders have a strong tendency to agglomerate. and it make difficult the compaction process and to achieve a good density. To exert control over the compaction process. the powders were spray dried to obtain spherical granules. Thus the stability of slurries of these powders was studied by adding ammonium polyacrylate (Duramax D3005) as dispersant and the suspension stability was measured by electrophoretic mobilities. Slurries prepared with the better conditions were dried in a laboratory scale spray dryer. The prepared granules were characterized by morphology observation (SEM). surface area (BET). Vickers hardness and sintered ceramics bodies density were measured.

Introduction

Fuel cells are an alternative to generation of electric power from chemical energy of fuels. Among few kinds of cells, Solid Oxide Fuel Cells (SOFC), made with ceramic components has been proposed for large scale generation, due to its high efficiency in conversion of energy, possibility of use of different fuels and low emission of pollutant gases, among other advantages. A cell is basically composed by three components, the solid electrolyte and two electrodes. The most studied material for the electrolyte are ceramics made of fully stabilized zirconia, preferably yttria stabilized zirconia (YSZ). The key feature needed is a high ionic conductivity in a dense and gas tightens ceramic made as thin layers. To assure these properties, ceramic raw materials must have homogeneous chemical composition and suitable physical characteristics [1]. In the classical ceramic processing, by press forming followed by firing, powders aggregated as spherical granules has many advantages as higher final densities, ease of compaction, reproducible procedures and rapid production. One of the proposed methods is to prepare a stable aqueous suspension of the powders followed by a controlled drying process.

Spray drying is the most widely used method to remove solvent from a fluid material containing solids. The contact of this feed material, in a form of small drops formed by atomizing, with a large volume of hot gases leads to a high mass transfer rates, resulting in short dry times with minimum thermal degradation[2.3]. The shape and size of these granules are determined by spraying conditions, physical characteristics of powders and composition of the slurry [4]. This composition includes the ceramic powder, a solvent which is most commonly water and organic additives as dispersants and binders. The slurry viscosity strongly affects the size distribution and shape of the granules. Uniform solid spheres are the ideal granule shape for most ceramic systems. Recent studies attributed the formation of solid granules to a low dispersants level and the formation of hollow granules to a high dispersant level [5,6]. During the drying process, droplet reach an equilibrium temperature with the drying gas and solvent evaporates. The surface of the droplet dries first and form a solid external shell. When the yield stress of the suspension is low, particles can

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rearrange and migrates carried by the solvent. forming a dense shell and leaving an internal void. But when particles are flocculated, migration is difficult and a continuous network of particles and a spherical and porous granule can form. Based in the above described considerations, this work shows the results of a series of experiments of spray drying of a suspension of YSZ synthesized by a wet chemical coprecipitation process and the characterization of the obtained ceramics powders .

Experimental procedures

YSZ powders were synthesized by a coprecipitation route and details of the process are described elsewhere [7]. Briefly, it consists of a mixture of solution of zirconium oxychloride (Ipen 99.8% ZrO_2) and yttrium chloride (Aldrich 99.99% Y_2O_3). that are slowly added to a 50% solution of ammonium hydroxide, followed by washing. drying with organic solvent, azeotropic distillation, calcination in a muffle furnace and milling. Aqueous slurry with 15 vol% of solids (50 wt%) were made using PAA (Duramax 500 Rohm and Haas) as anionic dispersant and PVA (CAAL) as binder. Powder surface area was determined by a N_2 gas adsorption (Quantachrome) and particle/agglomerate size were evaluated by Laser diffraction method (Cilas). The flocculation state was evaluated from its electrophoretic mobility, measured with a ZetaPALS (Brookhaven) and viscosity was measured with a DV-III rheometer (Brookfield). Drying experiments were done in a laboratory scale cocurrent Spray dryer model B 190 (Buchi). Ceramics were uniaxially compacted as cylindrical pellets and sintered at 1500°C for 01 hour. Powders morphology and ceramic microstructure were observed by SEM in a XL 30 microscope (Phillips). Ceramic hardness and fracture toughness were measured in a VMT-7 Vickers indenter (Buehler).

Results

In figure 01, SEM micrograph of the as synthesized powders are shown. It is formed by small particles with mean particle size of 2.6 μm and specific surface area is about $60m^2.g^{-1}$. Variation of zeta potential with the increase of PAA concentration is plotted in figure 02. Zeta potential increases from pure suspension up to 2 wt% PAA, and little or no effect is observed above this value.

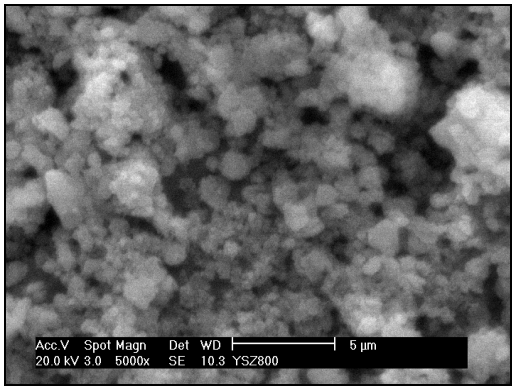

Fig. 01. SEM micrograph of YSZ powder.

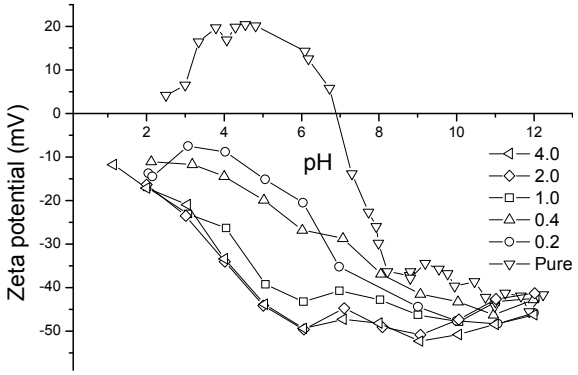

Fig. 02. Zeta potential of slurries varying PAA concentration

Viscosity of suspensions with 2wt% PAA, measured as a function of solid content are presented in Figure 03, showing that viscosity is relatively low to PAA content of about 40wt% and became high for 60wt%. The plot of the viscosity of a suspension with fixed solid content (60 wt%) as a function of PAA concentration are shown in figure 04. It is observed that viscosity is relatively low from 1.0 to 2.0wt%PAA, and is higher for 4.0wt%.

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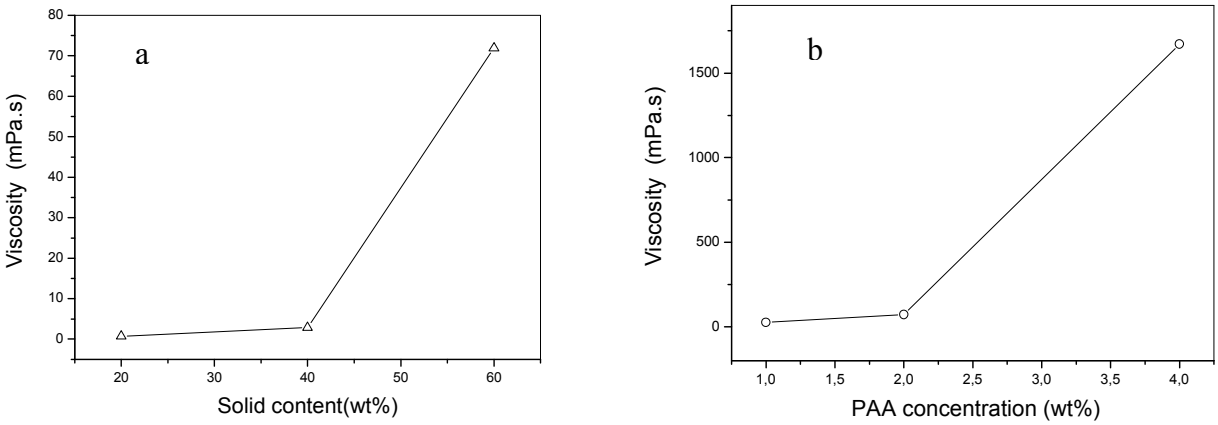

Fig. 03. Viscosity of suspensions with (a) 2wt%PAA as a function of solid content, and (b) 60wt% solids as a function of dispersant amount.

From these results and adopting concentrations used in works that studied slurries of zirconia powders[3,8], the following conditions were fixed: powder concentration at 15 vol% (50 wt%). pH of suspension to 10.4 and the PVA to 0.5 wt%. Slurries were prepared with PAA concentration of 1.0 and 2.0wt%, to observe different states of flocculation. Micrographs of granules are presented in figure 04.

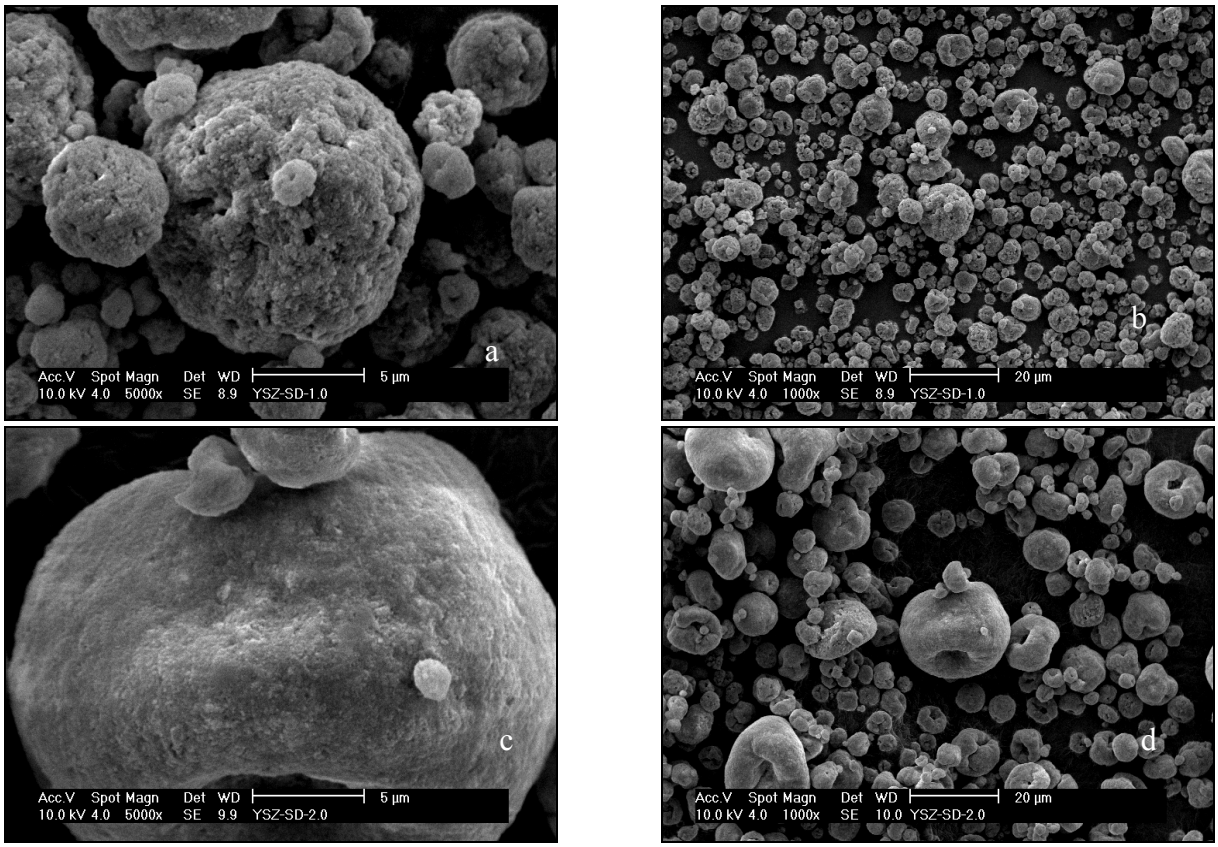

Fig. 04. Granules obtained from slurries with 1.0 wt% (a) and (b), and 2.0 wt% (c) and (d) of PAA.

Samples obtained with 1.0wt% PAA seem to be porous and the size is smaller and relatively homogenous. By its turn, samples from slurries with 2.0 wt%PAA is apparently denser and granules size distributed in a larger range. The number of granules with defects as voids and irregular shapes are higher in the last case. Specific surface areas of these two powders are presented in table 01.

Comparison with powders without spray drying treatment shows that sample with 1.0 wt% of PAA have higher specific surface area and sample with 2.0 wt% have smaller surface area.

Table 01. Specific surface area of Spray-dried powders.

Sample [wt% PAA]	Spray drying treatment	Specific Surface area [$m^2.g^{-1}$]
0.0	no	58.7
1.0	yes	66.4
2.0	yes	46.1

Densities of pressed ceramic pellets samples are compared to those prepared from powders without spray drying treatment, as shown in table 02. Sample with 2.0 wt% PAA has lower density but there is no significant difference between the two others. SEM micrographs of YSZ ceramics without spray drying treatment are presented in Figure 05, in the form of fractured (a) and thermally-etched (b) samples.

Table 02. Comparison of densities of ceramics sintered at 1500°C for 01 hour, for Spray –dried powders and powder without treatment.

Sample [wt% PAA]	Spray drying treatment	Apparent density [g. cm^{-3}]	% Theoretical density*
0.0	no	5.84	96.4
1.0	yes	5.76	95.9
2.0	yes	5.57	92.7

*Referred to Cubic zirconia symmetry with 6.01 g. cm^{-3}.

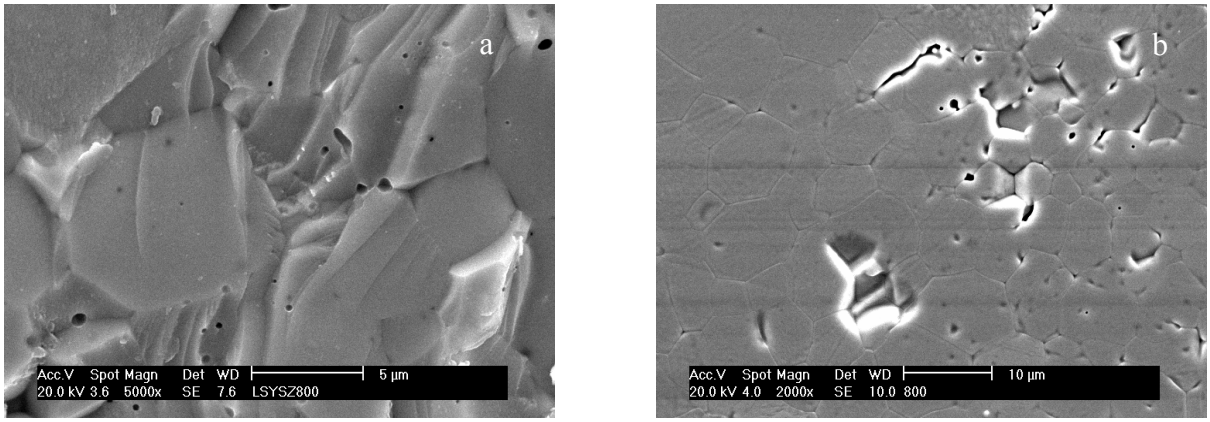

Fig. 05. SEM micrographs of fracture surface (a) and thermally etched surface (b) of ceramics prepared from powders without spray drying treatment.

SEM micrographs spray dried samples with 1.0 and 2.0 wt% of PAA are presented in Figures 06 and 07. Samples obtained from slurries with 2.0wt% PAA have more porosity than that with 1.0wt%PAA, in agreement with density values. Although densities are very similar, microstructures showed some differences. Ceramics prepared from powders without spray drying have grain size around 10 microns while samples prepared from spray dried powders have grain

size of about 5 microns and particularly for the sample with 1.0 wt%PAA, pores are smaller and more uniformly distributed.

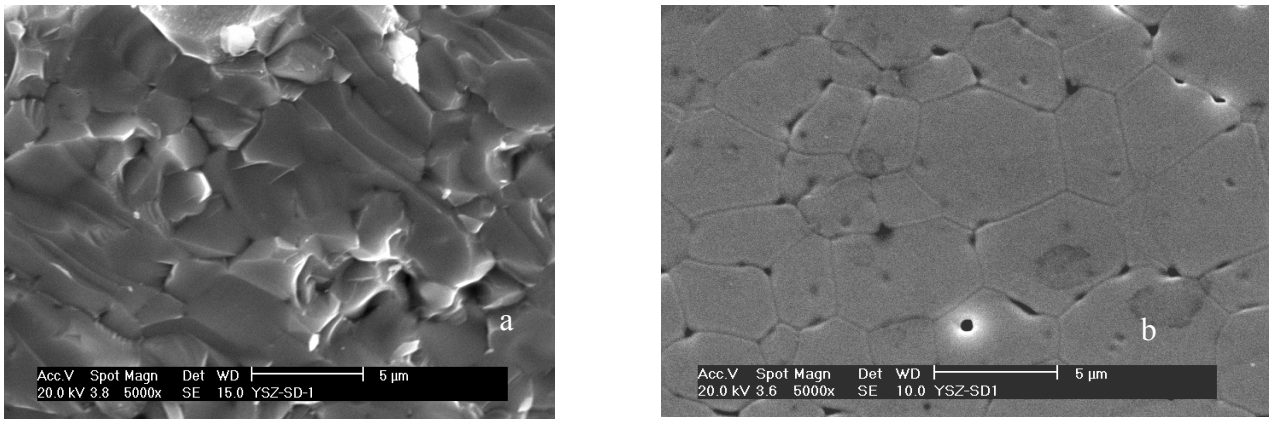

Fig. 06. SEM micrographs of fracture (a) and thermally etched (b) surface of ceramics prepared from spray drying of suspension with 1.0wt%PAA.

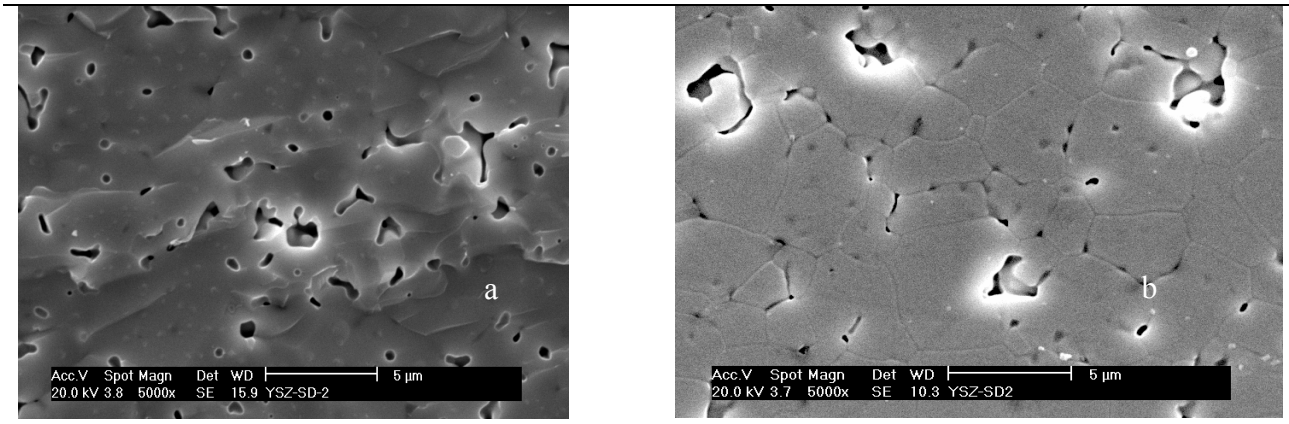

Fig. 07. SEM micrographs of fracture (a) and thermally etched (b) surface of ceramics prepared from spray drying of suspension with 2.0wt%PAA.

Vickers hardness and fracture toughness of samples are presented in table 03. Hv values obtained for sample with 1.0 wt% PAA is higher compared to that obtained for sample with 2.0 wt% PAA and without spray drying, and the fracture toughness is lower.

Table 03. Vickers hardness of samples.

Sample [wt% PAA]	Spray drying treatment	Vickers hardness [GPa]	Fracture toughness [MPa.m.$^{1/2}$]
0	no	9.4±2.0	-
1	yes	11.5±0.3	1.4±0.1
2	yes	9.6±0.4	1.7±0.2

Conclusions

In this work we confirmed that spray drying is an efficient method to dry YSZ ceramics and to produce granules of near spherical shapes. The shape and size of granules are highly influenced by the flocculation state of the slurry of ceramic powder. Although suspensions has to be stable and uniform, the lower is its viscosity, the more are the defects as voids and irregular shapes in the

granules. Best results were obtained for slurries prepared with 1 wt% PAA. Ceramics densities are not significantly different when compared to ceramics prepared from powder without spray dryer treatment, but microstructure seems to be formed by smaller grains and more uniform. Vickers hardness is higher for sample with 1.0wt%PAA when compared to samples with 2.0wt%PAA and samples without spray drying. Studies with suspensions with lower dispersant concentration are planned.

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