A STUDY ON DENSIFICATION OF YTTRIA-STABILIZED ZIRCONIA SYNTHESIZED FROM GLYCINE-NITRATE PROCESS AND SINTERED UNDER DIFFERENT CONDITIONS [1]

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Abstract
Nanocrystalline 8mol% yttria stabilized zirconia powders (8YSZ) were prepared by the glycine-nitrate process (GNP), which consists of the redox reactions between the respective metal nitrates and glycine in a preheated furnace at 600°C. A series of 8YSZ powders were synthesized by altering the glycine/metal oxides ratio (G/O). These nanocrystalline powders, with an average crystallite size of 15-18 nm, were used to prepare dense ceramics. The effect of different sintering regimes and compacting method on the density and microstructure of the sintered YSZ was determined using density measurements and scanning electron microscopy (SEM). The results revealed that the properties of the as-synthesized powders are influenced by the molar ratio G/O, with the ratio increasing from 0.23 to 2, the crystallite sizes increase slightly from 15.4 to 17.5 nm. Green bodies conformed by cold isostatic pressing showed the highest degree of densification. The results of the SEM and densification degree indicate high porosity because of the elimination of gas during combustion method. The best result in terms of densification was obtained for YSZ.G1, however, for a better comparison of the results, it is necessary to sinter all pellets in the same conditions.
Keywords: YSZ ceramics; Densification; Sinterization; Combustion method.

ESTUDO SOBRE A DENSIFICAÇÃO DE CERÂMICAS DE ZIRCÔNIA ESTABILIZADA COM ÍTRIA SINTETIZADAS PELO PROCESSO GLICINA-NITRATO E SINTERIZADAS SOB DIFERENTES CONDIÇÕES

Resumo
Pós de zircônia estabilizada com ítria (8YSZ) foram preparados pelo método de combustão segundo o processo glicina-nitrato, mediante reações redox entre os respectivos nitratos metálicos e glicina em um forno pré-aquecido a 600°C. Diversas amostras de 8YSZ foram sintetizadas alterando-se a razão entre os óxidos metálicos e a glicina (O/G). Os pós nanocristalinos produzidos, com tamanho médio de cristalito na faixa 15-18 nm, foram usados na confecção de cerâmicas densas. Os efeitos das diferentes condições de conformação e sinterização sobre a densidade relativa e a microestrutura das amostras analisadas foram estudados utilizando-se medidas de densidade e microscopia eletrônica de varredura (MEV). Os resultados mostram que as propriedades dos pós sintetizados sofrem a influência da relação molar G/O, que paralelamente ao aumento da relação de 0,23 para 2, ocorre um ligeiro aumento dos tamanhos de cristalitos de 15,4 para 17,5 nm. Os compactos a verde conformados em prensa isostática mostraram maiores valores de densidade relativa. As fotomicrografias e as densidades relativa mostraram alta porosidade devido à eliminação de gases durante a queima. O melhor resultado em termos de densificação foi obtido para a amostra YSZ.G1, sendo que para melhor comparação dos resultados se faz necessário sinterizar as pastilhas nas mesmas condições.
Palavras-chave: YSZ; Densificação; Sinterização; Método da combustão.

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INTRODUCTION

The solid oxide fuel cell (SOFC) is one of the most promising technologies for the production of electric energy, due to the highest degree of efficiency, low emissions of pollutants, silent work (absence of the movable mechanical parts), wide variety of fuels that can be processed, the arising heat at high temperatures can be used in many different ways and relative simplicity of such devices.[1]

Each unit cell for the SOFC includes yttria stabilized zirconia (YSZ), containing typically 8mol% Y_2O_3, as the electrolyte; a ceramic-metal composite (cermet) comprised of Ni and YSZ as the anode; lanthanum strontium manganite (LSM) as the cathode; the interconnect material is alkali doped lanthanum chromite ($LaCrO_3$); and glasses or glass-ceramics system as sealant for planar design.[2]

The efficiency of energy conversion and durability of performance mainly depend on the oxide ion conducting solid electrolyte activity. In this context, the yttria-stabilized zirconia (YSZ) is one of the most popular materials employed as electrolyte in solid oxide fuel cell due to its pure ion conductivity, good chemical compatibility, excellent mechanical properties, stability in dual environment (oxidizing and reducing) and thermal stability.[3]

Different processing methods have been developed for the production of nano-crystalline YSZ, such as co-precipitation technique,[4] sol-gel preparation,[5] hydrothermal synthesis,[6] sonochemical process[7] and Pechini method.[8] However, these reactions are complicated, they require multi-step reaction routes and/or long processes. Recently, combustion synthesis have shown to be an attractive method for preparing multicomponent oxide powders that are crystalline, homogeneous, high-purity and have a narrow particle size distribution.[9]

Briefly, the combustion synthesis technique consists essentially of self-propagating high temperature synthesis. This method is based on the principle of explosive decomposition of nitrate reagents and fuel mixtures to produce a spontaneous flame with no controlled temperature leading in a short time to a foamy but well crystallized single-phase powder.[10]

In a previous paper, Wang et al.[11] investigated the effect of glycine quantity on YSZ characteristics. YSZ powders were prepared with glycine from 70% to 120% of stoichiometric amount. The results showed that the crystallite size of YSZ increases with the amount of glycine and heating temperature. This occurs because of the flame temperature of the glycine-nitrate combustion reaction that increases with glycine quantity. High temperature leads to further crystalline growth. Besides, powders prepared with low glycine quantity are much easier to be densified.

He, He e Wang[12] evaluated the effects of 1:1 and 1:2 molar ratio of metal ions to glycine (denoted as M/G) and heat-treatment conditions on synthesis, sintering and properties of nano-sized YSZ powders. It was reported that when the M/G ratio was 1:1 the maximum sintered density was attained by pre-sintering at 1000 or 1200°C for 6h and sintering at 1450°C for 6h. When the M/G ratio was 1:2 the maximum sintered density was attained by pre-sintering at 1000°C or 1200°C for 6h and sintering at 1400°C for 6h; sintering temperature above 1400°C causes a decrease of the relative density.

An important requirement for potential electrolyte materials is the density. The sample's density reflects the electrical and mechanical properties. However, to our knowledge, it is difficult to obtain a dense yttria stabilized zirconia ceramic. Thus, the aim of this work is to characterize and evaluate the microstructural densification of bulk YSZ materials prepared from chemical synthesized powders. The phase

identification, particle morphology, average crystallite size and sintering characteristics of the YSZ powder are reported and the optimal conditions to prepare YSZ electrolyte with high density were determined. The scope of this study is focused on to evaluate the effects of: (i) different molar ratio of metal oxide/glycine (O/G), (ii) sintering conditions and (iii) compaction method on the density of YSZ materials.

EXPERIMENTAL

For the combustion synthesis of 8mol%Y_2O_3-stabilized zirconia (8YSZ) powder, zirconyl nitrate hydrate ($ZrO(NO_3)_2.6H_2O$, Acros Organics, 99.5%), yttrium nitrate ($Y(NO_3)_3.6H_2O$, Acros Organics, 99,9%) and glycine (Vetec) were dissolved in small amount of water. The homogeneous powder mixtures, with glycine/metal oxides ratio (G/O) of 1 and 2, were heated on a hot plate at 150°C and it was converted to a viscous gel due to evaporation of water. The mixture was then heated in a muffle furnace at 600°C until self-ignition. The resulting fine powders were calcined at 900°C for 6h using heating rates of 10°C/min, with air flow rate of 60 mL/min. The powder was pressed into pellets of 12.4 mm in diameter and 2.1 mm in thickness at a pressure of 200 MPa. The discs were sintered under different conditions of temperature and time. The nanocrystalline powder with glycine/oxide ratio of 0.23 was prepared as previously described by Kaus et al. [13] using smoldering combustion method.

The amount of glycine for the formation of YSZ can be calculated based on the total oxidation and reduction valencies of the components. According to the concept used in the propellant chemistry, the elements C and H are considered as reducing elements with the corresponding valencies +4 and +1, oxygen is considered an oxidizing element with the valency -2, and nitrogen is considered with valency zero. The metals such as Y and Zr are also considered as reducing elements with the corresponding valencies +3 and +4, respectively.[14] Therefore, the amount of glycine required for combustion is calculated using empirical formula for the oxides.[15] The samples studied are denoted YSZ.G1, YSZ.G2 and YSZ.G023, where G represents the fuel (glycine) and the numbers (1, 2 and 0.23) represent the ratio G/O.

Crystalline phase evolution of the resulted powder was detected by X-ray diffraction (XRD) analysis with a PANalytical X'Pert PRO diffractometer using Cu Kα-radiation (λ = 1.541806Å) with Ni filter and the data were collected from 20° to 100°. The chemical composition of the samples was characterized by X-ray fluorescence (XRF, Shimadzu, EDX-720/800HS). The simultaneous differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out using a Rigaku TAS-100 Model thermal analyzer. The thermal analyses were conducted at a heating rate of 10°C/min from 25 to 1000°C, under a flow of 15%O_2/N_2. The microstructures of the densified samples were examined by scanning electron microscopy (SEM, Jeol JSM-64602 LV) equipped with X-ray dispersive energy spectroscopy (EDS, Link ISIS, Oxford Instruments) for compositional analysis. The sintered discs were polished, then chemical etched by immersing in HF or H_3PO_4 solutions for 1-30 minutes or thermal etched for 12 min at temperature 50°C below sintering temperature was used. The density of the sintered sample was measured by the Archimedes method (Mettler AE-200 analytical balance) using distilled water.

RESULTS AND DISCUSSION

The elemental composition of the calcined 8YSZ was determined by XRF and shown in Table I. These compositions are satisfactorily close to those initially desired and based on the precursor mixture.

Table I – Quantitative XRF data showing the molar composition.

Sample	Y_2O_3 (% mol)	ZrO_2 (% mol)
YSZ.G023	7.80	92.2
YSZ.G1	7.85	92.15
YSZ.G2	7.42	92.58

Figure 1 shows the X-ray diffraction patterns of 8 mol% yttria-stabilized zirconia (YSZ) powders synthesized by the combustion process with various glycine contents. As shown in Figure 1, a good crystallite state was observed for all samples after calcination, indicating the formation of a single-crystalline cubic phase, according to 030-1468JCPDS card. The calculated 'd' values match with the reported yttria stabilized cubic zirconia having a composition $Y_{0.15}Zr_{0.85}O_{1.93}$ and the lattice parameter 'a' was estimated to be 5.139 Å. Approximate crystallite sizes were calculated using data from the X-ray diffraction patterns and the Scherrer's equation (Eq. 1) based on full width at half maximum (FWHM) of c-YSZ (111) peaks.

$$L = 0.9\,\lambda / (\beta.\cos\theta) \qquad \text{(Eq.1)}$$

where L is the crystallite size, λ is the wavelength of the filament used in the XRD machine, β is the width of a peak at half of its intensity and θ is the diffraction angle of the same peak.

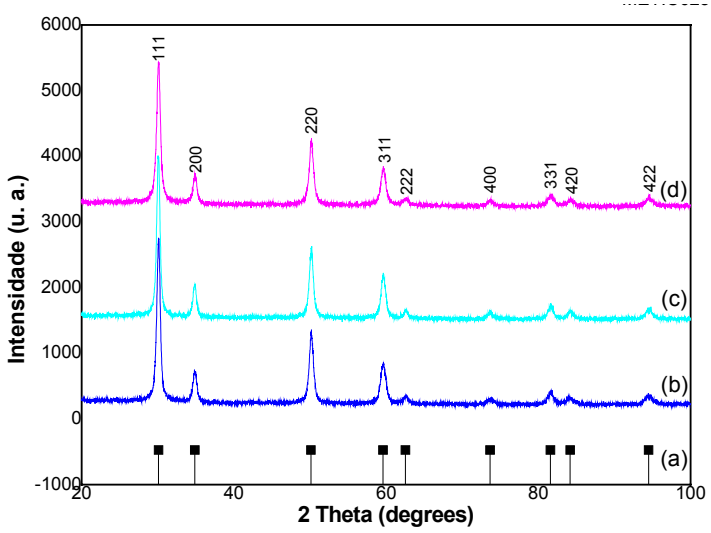

Figure 1. Powder X-ray diffraction patterns of YSZ calcined samples: (a) JCPDS card no.: 030-1468, (b) YSZ.G1, (c) YSZ.G2 and (d) YSZ.G023.

The average crystallite sizes calculated for each sample and the full-width at half maximum (FWHM) of the reflections are given in Table 2. It can be seen that the crystallite size slightly increases with the amount of glycine. It can be inferred that the flame temperature of the glycine-nitrate combustion increased with glycine

quantity.[11] Results showed that nanocrystalline YSZ powders were synthesized using glycine-nitrate process.

Table 2 - The full-width at half maximum (FWHM) and average crystallite sizes of the samples studied.

Sample	FWHM (°)	Average crystallite size (nm)
YSZ.G023	0.572032	15.443
YSZ.G1	0.526325	16.783
YSZ.G2	0.503570	17.542

The sintering temperature and time, and densification degrees in percentage of the respective theoretical density for the pellets prepared by only uniaxial pressing and prepared by uniaxial pressing followed by cold isostatic pressing are summarized in Table 3. According to the results showed, the relative density decreased when more glycine is used, in the case of G/O ratio of 1 and 2. This behavior can be associated with the fact that more glycine causes coursing of the particles, which are generally harder to be densified than fine particles. Moreover, the best densification level was achieved when the ceramic discs were prepared by uniaxial formation followed by isostatic pressing.

It is important to point out that the conditions of sintering used were chosen based on the high densification level reported in literature searched. However, for a better comparison of the results, it is recommended to sinter all pellets in the same conditions.

Table 3 - The conditions of sintering, the densification degrees for the pellets prepared by only uniaxial pressing and prepared by uniaxial pressing followed by cold isostatic pressing.

Sample	Densification degree (%)		Sintering Conditions
	Uniaxial	Isostatic	
YSZ.G023	72.15	92.3	1500°C/6h and 1400°C/4,5h
YSZ.G1	82.2	93.96	1000°C/6h, 25°C/6h and 1450°C/6h
YSZ.G2	----	88.93	1000°C/6h and 1450°C/6h

Figure 2 (a-c) shows the thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTGA) and differential scanning calorimetry (DSC) of the studied systems. The TGA pattern shows that the weight loss takes place in several steps. The total weight loss for the samples was 13.7, 9.5 and 7.8 wt%, respectively, for the YSZ.G023, YSZ.G1 and YSZ.G2. This behavior can be explained considering that the increase in quantity of the glycine leads to an increase of temperature of combustion, therefore less amount of residual carbonate species.

Three different stages of decomposition may be described as follows. The first weight loss that occurred before 300°C is associated with the loss of physisorbed water and the removal of chemisorbed hydroxyl groups; the second stage occurred over a temperature range of 300°C-550°C, which can be attributed mainly to the decomposition process of the incomplete glycine combustion and the third stage above about 550°C is related to the decomposition of carbonate and nitrate residues.

The DSC curves show small endothermic peaks at about 100°C, which are attributed to the removal of water molecules adsorbed from the powders. There is a small exothermic peak at about 220°C in the DSC curves that can be associated mainly with the decomposition process of the residual organic matter, that is, the elimination of the incomplete glycine combustion. Finally, the peak at about 660°C in the DSC curves shows that the amorphous gel is completely converted to cubic fluorite-type structure of YSZ (12).

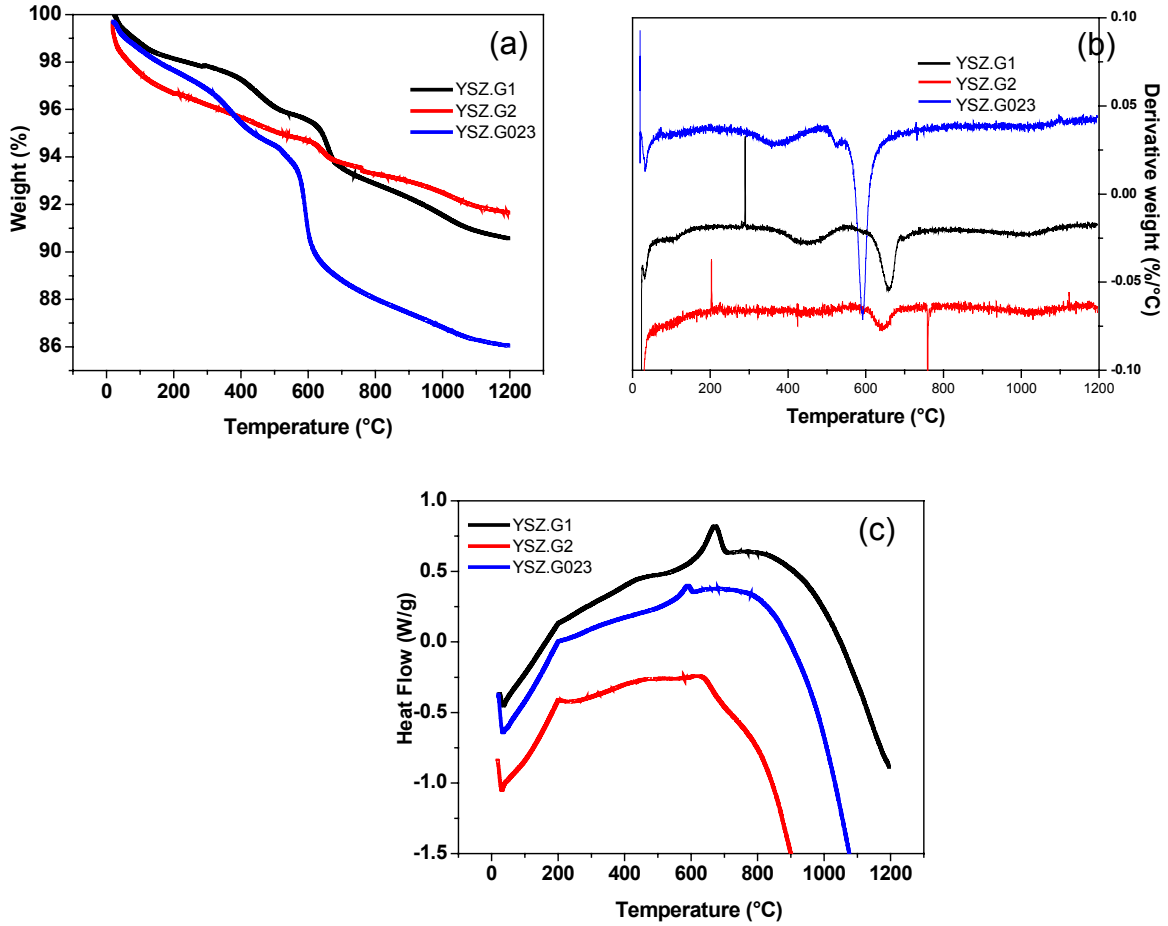

Figure 2. Thermal behavior including: (a) thermogravimetric analysis, (b) derivative thermogravimetric analysis and (c) differential scanning calorimetry of the precursor powders of the studied systems.

Figure 3 (a-c) show photomicrographies (SEM) of the ceramic nanopowders of the studied systems. Figure 3(a) and (c) show large agglomerates and irregular particles with a foamy aspect. Moreover, they present typical micrographs for synthesized powders by GNP method. This occurs because a large amount of gaseous material is evolved and hence the combustion product is highly porous, as shown in the SEM micrographs. In the Figure 3 (b) it can be clearly observed the formation of the some lamellar structure.

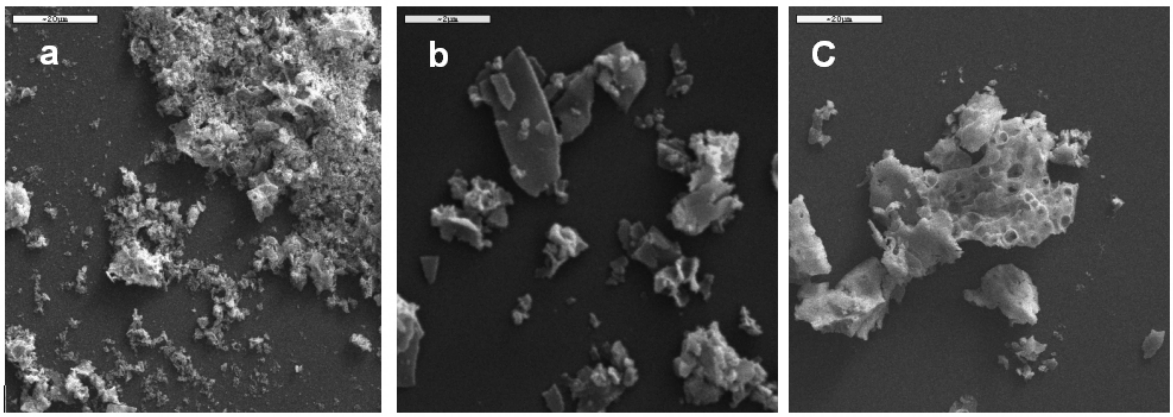

Figure 3. SEM micrographs of ceramic powders of (a) YSZ.G023 (bar = 20 μm) (b) YSZ.G1 (bar = 2 μm) and (c) YSZ.G2 (bar = 20 μm).

Figure 4 (a) show photomicrographies of the microstructures of the sintered cross section of the YSZ.G1 pellets without any treatment. In image can be observed dense grain boundary regions and homogenous microstructure with narrow grain size distribution. The microstructures of sintered pellets after thermal or chemical etching are shown in Figure 4 (b) and (c) respectively. After the etching process, the grain boundary images are not more observed, probably because it has not yet been determined the best etching conditions. Based on the SEM images, it can be seen that in this conditions of sintering the sample achieved low porosity and consequently high densification degree corroborating the results obtained through Archimedes method (Table 3).

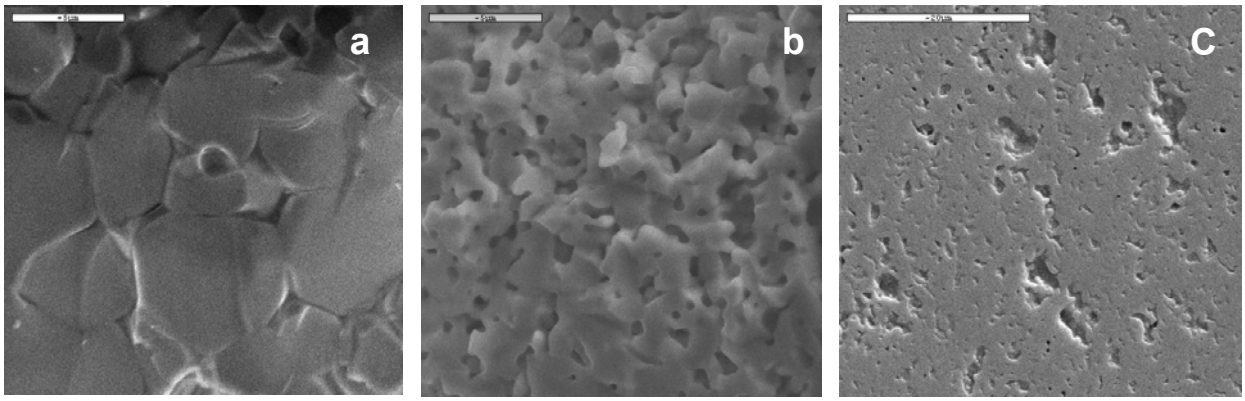

Figure 4. Photomicrographies of the microstructures of the sintered cross section (fractured surface) of the YSZ.G1 pellets: (a) without any treatment (bar = 5 μm), (b) thermal etched (bar = 5 μm) and (c) polished and chemical etched surface (bar = 20 μm).

CONCLUSIONS

The glycine-nitrate combustion synthesis is a simple and convenient method to prepare 8YSZ powders using precursor containing metal nitrates and glycine dissolved in water, with production of nanocrystalline cubic phase with average crystallite size in the range of 15 nm -18 nm.

The effect of different glycine/metal oxides ratios on the microstructure of YSZ electrolyte was investigated by XRD, SEM, thermal analysis and density analysis. The three studied cases showed the same thermal behavior. The obtained experimental results suggest that the relative density decreased when more glycine was used; it might be due to the increasing glycine amount caused the coursing of the particles, which are generally harder to be densified than fine particles. Green compacts conformed by cold isostatic pressing showed the highest degree of densification. Microstructure with full density is an essential prerequisite for a high performance of the fuel cell electrolyte.

In future work, we will carry out the sintering of the pellets in the same conditions since sintering behavior of ceramic materials dependent of the sintering condition, therefore, different sintering temperature and time will result in diverse relative density.

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REFERENCES

1 EG&G TECHNICAL SERVICES, INC., Fuel Cell Handbook (Seventh Edition), U.S. Department of Energy, Morgantown, WV, 2004.

2 WEBER, A., IVERS-TIFFÉE, E. Materials and Concepts for Solid Oxide Fuel Cells (SOFCs) in Stationary and Mobile Applications, **Journal of Power Sources**, v. 127, p. 273-283, 2004.

3 SINGHAL, S. C., KENDALL, K. High temperature solid oxide fuel cells: fundamentals, design and applications, Elsevier, 2004.

4 XIA, C., ZHA, S., YANG, W., PENG, R., PENG, D., MENG, G. Preparation of Yttria Stabilized Zirconia Membranes on Porous Substrates by a Dip-coating Process, Solid State Ionics, v. 133, p. 28, 2000.

5 KESHIMIRI, M., KESLER, O. Colloidal Formation of Monodisperse YSZ Spheres: Kinetics of Nucleation and Growth, **Acta Materialia**, v. 54, p. 4149-4157, 2006.

6 DELL'AGLI, G., MASCOLO, G. Zirconia-yttria (8 mol%) Powders Hydrothermally Synthesized from Different Y-based Precursors, **Journal of the European Ceramic Society**, v. 24, p. 915-918, 2004.

7 MENZLER, N. H., LAVERGNAT, D., TIETZ, F., SOMINSKI, E., DJURADO, E., FISCHER, W., PANG, G., GEDNANKEN, A., BUCHKREMER, H. P. Materials Synthesis and Characterization of 8YSZ Nanomaterials for the Fabrication of Electrolyte Membranes in Solid Oxide Fuel Cells, **Ceramics International**, v. 29, p. 619-628, 2003.

8 LABERTY-ROBERT, C., ANSART, F., DELOGET, C., GAUDON, M., ROUSSET, A. Dense Yttria Stabilized Zirconia: Sintering and Microstructure, **Ceramics International**, v. 29, p. 151-158.

9 HAN, S. D., KHATKAR, S. P., TAXAK, V. B., KUMAR, D., PARK, J., Combustion Synthesis and Luminescent Properties of Eu^{3+}-doped $LnAlO_3$ (Ln = Y and Gd) Phosphors, **Materials Science and Engineering B**, v. 127, p. 272-275, 2006.

10 SOUSA, V. C., SEGADÃES, A. M., MORELLI, M. R., KIMINAMI, R. H. G. A. Combustion Synthesis ZnO Powders for Varistor Ceramics, **International Journal of Inorganic Materials**, v. 1, p. 235-241, 1999.

11 WANG, Q., PENG, R., XIA, C., ZHU, W., WANG, H. Characteristics of YSZ Synthesized with a Glycine-nitrate Process, **Ceramics International**, *in press,* 2007.

12 HE, T., HE, Q., WANG, N. Synthesis of Nano-sized YSZ Powders from Glycine-nitrate Process and Optimization of their Properties, **Journal of Alloys and Compounds**, v. 396, p.309-315, 2005.

13 KAUS, I., DAHL, P. I., MASTIN, J., GRANDE, T., EINARSRUD, M. Synthesis and Characterization of nanocrystalline YSZ powder by smoldering combustion synthesis, **Journal of Nanomaterials**, p. 1-7, 2006.

14 RINGUEDÉ, A., LABRINCHA, J. A., FRADE, J. R. A Combustion Synthesis Method to Obtain Alternative Cermet Materials for SOFC Anodes, **Solid State Ionics**, v. 141-142, p. 549-557, 2001.

15 SATHIYAMOORTHI, R., SUBRAMANIA, A., GANGADHARAN, R., VASUDEVAN, T. Preparation of Nanoparticle Size $LiBiO_2$ by Combustion Method and its Electrochemical studies for Lithium Secondary Cells, **Pramana - Journal Physics**, v. 65, p. 973-980, 2005.