

Combustion Synthesis of NiO/YSZ Composite

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Abstract. Nickel oxide-yttria stabilized zirconia (NiO-YSZ) anode materials were synthesized by combustion process involving metal nitrate-urea decomposition. The precursor was heated to evaporate water undergoing dehydration, and then the mixtures froth and swell. Further heating produces large amounts of gases that ignite at ambient atmosphere. Different nitrate/urea initial molar ratios were employed in order to investigate the influence of the reaction temperature in the physical characteristics of the powder composite. The flame temperature was measured by infrared optical pyrometer. The combustion was rapid and self-sustaining, with flame temperatures ranging from 870 to 1330°C. The as-synthesized powders were uniaxially pressed and sintered in air. Powders were characterized by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), helium pycnometry for density measurements and gas adsorption technique (BET). The ceramic samples were evaluated by SEM and Archimedes density measurements.

Introduction

A Solid oxide fuel cell (SOFC) is an environmentally friendly energy conversion system in which a gaseous fuel and an oxidizing gas are combined electrochemically to generate electricity and heat. One of the most important tasks in SOFC research is the reduction of operating temperature from 900-1000°C down to 700-800°C, to reduce degradation of cell components, improve flexibility in cell design, and lower the material and manufacturing cost by the use of cheap and readily available materials. However, the electrolyte conductivity and electrode kinetics drop significantly with the lowered operating temperatures and the fuel cell performance becomes increasingly dependent on the characteristics of the electrodes [1,2]. With a thin electrolyte layer, the anode or the cathode must be thickened in order to support the cell. Since the electrochemical performance of the anode is nearly independent of its thickness, unlike the cathode, the anode supported cell is the preferred for the planar cell construction.

Significant effort has also gone into developing high performance electrodes since, in most cases; the electrode activity determines the reaction rate. It is essential to have suitable electrode materials in terms of chemical and mechanical stability, high conductivity, good catalytic activity and mechanical compatibility; however, it is equally important to develop an electrode structure that gives a large active area.

Ni cermet is a widely used anode material for SOFC. Yttria-stabilized zirconia (YSZ) component is usually added to the cermet to form the composite anode, in order to extend the electrochemical reaction area from the anode/YSZ interface deep into the whole anode [3]. Furthermore, the functions of YSZ particles in the anode are to support the nickel-metal particles, inhibiting coarsening of the metallic particles at the fuel cell operating temperature, and providing an anode thermal expansion coefficient acceptably close to those of the other cell components [4]. Therefore, it is crucial to obtain better morphology including larger TPB (Three Phase Boundary) composed of Ni and YSZ grains for the achievement of high-performance anode.

The solution combustion powder synthesis process allows mixing the reactants on the molecular level due the initial reaction media being in the aqueous solution, permitting precise formulation of

the desired composition. The high reaction temperature provides homogeneous phases with excellent crystallinity, without calcination steps [5]. One of the major parameters that determine the phase formation of the crystalline phases of NiO, YSZ and Ni⁰ powder is the ratio of fuel to metal nitrate in the combustion reaction. In the combustion process of the nitrate – urea mixture, the metal nitrates decompose in nitrous oxides and metal oxides while that the urea decomposes in NH₃, HCNO, CO₂ and H₂O. In this paper, the combustion synthesis, was used for preparation of homogeneous NiO-YSZ powders.

Experimental Procedure

Zirconium nitrate solution (IPEN, Brazil), yttrium nitrate hexahydrated (Aldrich Chemical Co, USA), nickel nitrate hexahydrated (Aldrich Chemical Co, USA) were used as cations precursors and urea (Casa Americana, Brazil) was used as fuel. Aqueous solution of nickel nitrate and appropriate amounts of yttria nitrate and zirconium nitrate aqueous solutions were mixed to produce a final composition corresponding to 8 mol% yttria stabilized zirconia containing 56 wt% NiO. The batches were calculated on basis 10g of NiO-YSZ.

For sample preparation, a stoichiometric molar ratio between nitrate and urea was adopted according to the possible following equations:



Stoichiometric compositions of the metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valencies of the components. This numerical coefficient for stoichiometric balance is known as equivalent ratio (Φ_e) [6]. The mixture is stoichiometric when $\Phi_e = 1$, fuel-lean when $\Phi_e > 1$, and fuel-rich when $\Phi_e < 1$.

In this investigation, the urea amount was fixed at: stoichiometric value, and excess corresponding to 2, 2.50, 2.75 and 3 of the calculated stoichiometric value. This parameter can be represented by the following Φ_e values: 1, 0.65, 0.57, 0.55 and 0.52.

The aqueous solution containing precursor and fuel was transferred into a cylindrical pyrex dish stirred and heated on a hot plate (~ 400°C). Initially, the solution boils and undergoes dehydration. At a certain reaction stage the mixture froth and swell, followed by decomposition with the evolution of large amounts of gases such as N₂, CO₂, and H₂O. Afterwards, very fast reactions take off and produce voluminous powders. The temperature of reaction was measured with optic pyrometer (minolta/land infra-red model cycl PS 52 thermometer - Land infrared Ltda England). Powders were characterized by X-ray diffraction for phase identification, scanning electron microscopy (XL30, Phillips) for observation of particle and agglomerate morphology, gas adsorption (Nova 1200, Quantachrome) for BET surface area measurements and helium pycnometry (Micromeritics, AccuPyc 1330) for density measurements.

Cylindrical specimens of 15mm diameter and 1 mm height were uniaxially pressed at 100MPa and sintered in air at 1450°C for 1 hour. The resulting ceramics were characterized by scanning electron microscopy for microstructure observation; density was evaluated by the Archimedes method, and porosity by ASTM C20-00. Theoretical density for composition was calculated as follows:

$$\rho_s = \rho_{\text{NiO}} \cdot V_{\text{NiO}} + \rho_{\text{YSZ}} \cdot V_{\text{YSZ}} \quad (4)$$

where ρ_s , ρ_{NiO} and ρ_{YSZ} are theoretical density of NiO, YSZ, respectively, and V_{NiO} and V_{YSZ} are the volume fractions of NiO and YSZ.

Results and Discussion

The equivalent ratio (Φ_e), surface area (BET), measured flame temperatures, color of powders and the powder density are given in Table 01.

Table 1 – Characteristic of synthesized powders properties with different oxidant-to-fuel ratio

Sample Code	Φ_e	Sw [m ² /g]	Reaction Temperature [°C]	color	Density [g/cm ³]
NYSZ-1.0	1.0	130.34	-----	Black	4.37
NYSZ-2.0	0.65	87.02	865	Black	4.72
NYSZ-2.5	0.57	14.83	1151	Green	5.67
NYSZ-2.75	0.55	8.02	1283	Green	6.08
NYSZ-3.0	0.52	4.55	1329	Green	6.00

Fig. 1 shows the XRD of the NiO-YSZ powders produced at five different ratios of urea to nitrates. When stoichiometric and twofold stoichiometric urea was used as fuel, the amorphous phase were found in the as-burnt powders (Fig. 1(a) and 1(b)) and a higher surface area was attained as well as a finer particle size. This reveals a fuel-lean solution probably due the fact that during the heating solution a significant amount of nitrates evaporate. The other possibility is probably due to the fact that the self-generate heat is not sufficient to raise the temperature after ignition. Excess urea is thus often used. By increasing the excess of urea, powder crystallization occurs (Fig. 1(c), 1(d) and 1(e)) [7,8].

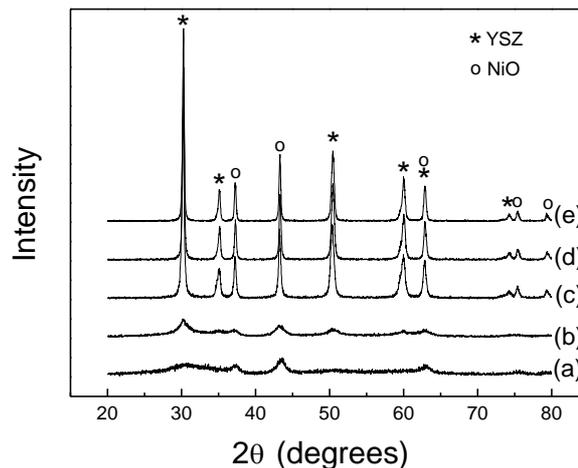


Fig. 1 - XRD patterns of NiO:YSZ synthesized powders as a function of the oxidizing to reducing (fuel) elemental composition ratio: (a) $\Phi_e = 1.0$, (b) $\Phi_e = 0.65$, (c) $\Phi_e = 0.57$, (d) $\Phi_e = 0.55$ and (e) $\Phi_e = 0.52$

Fig. 2 gives the scanning electron microscopy (SEM) images of these five samples. For $\Phi_e = 1.0$, the powder is formed by large porous agglomerates that are relatively voluminous with foamy aspect, as can be observed in Fig 2(a). The pores and voids are produced by the fast expulsion of gases during the combustion. In the others ratios of the oxidizing to reducing (fuel) elemental

composition, the as formed aggregates contain porous foam like islands which surface was perforated by a large number of pores, with a complex large surface area network structure. These porous aggregates can be easily crashed by ball milled

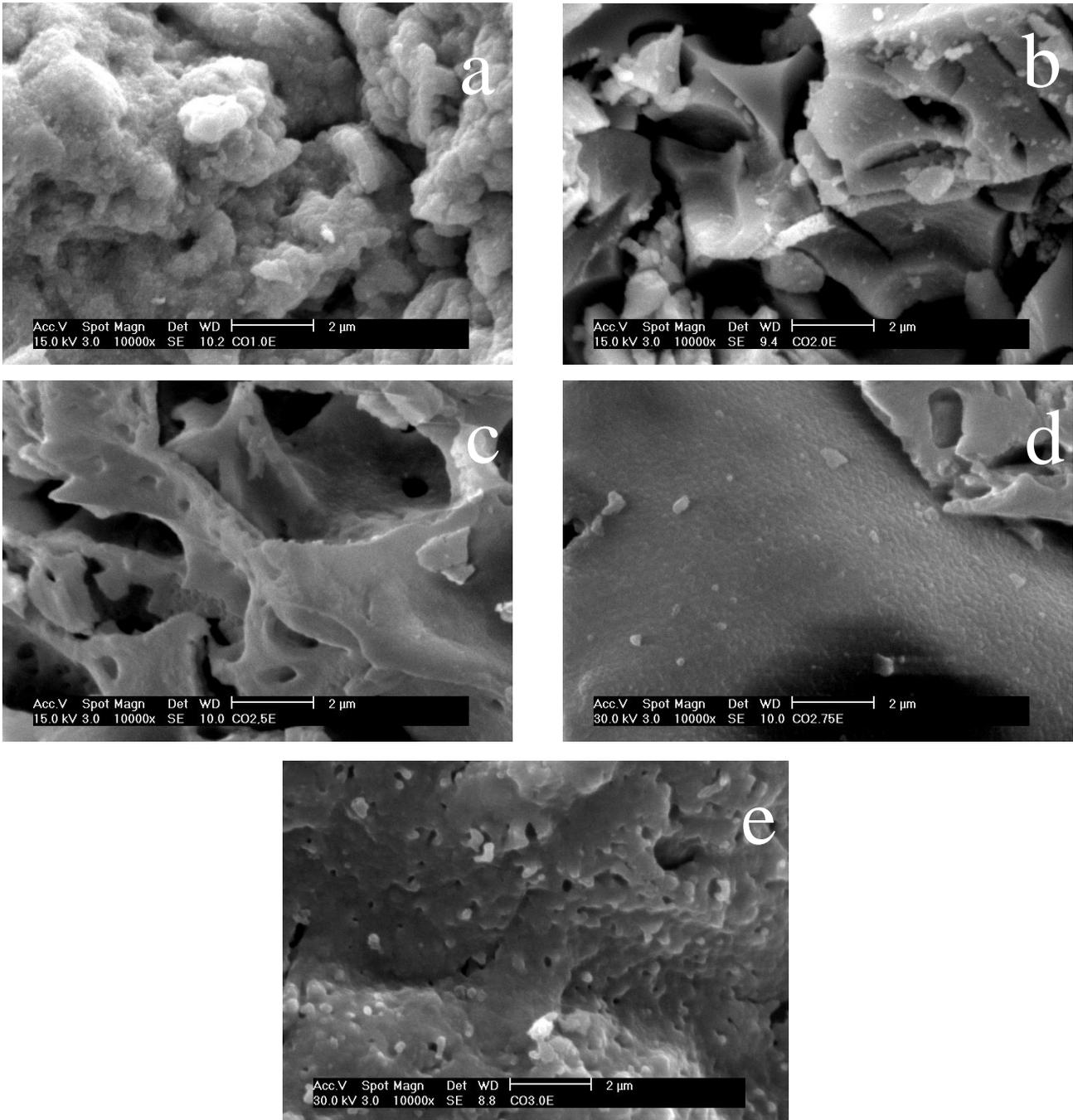


Fig. 2 – SEM micrographs of NiO:YSZ as synthesized powders as a function of the oxidizing to reducing (fuel) elemental composition ratio: (a) $\Phi_e = 1.0$, (b) $\Phi_e = 0.65$, (c) $\Phi_e = 0.57$, (d) $\Phi_e = 0.55$ and (e) $\Phi_e = 0.52$

Fig. 3 shows that the higher agglomerate mean size (43 μm) of oxide powder was produced for the stoichiometric ratio of the oxidizing to reducing (fuel) elemental composition. For powders synthesized in precursor solution contained twofold urea excess, the higher agglomerate mean size

is 38 μm . Employing the fuel-rich solution condition, the agglomerate mean size of oxide powders increases with increasing temperature combustion from 26 to 32 μm .

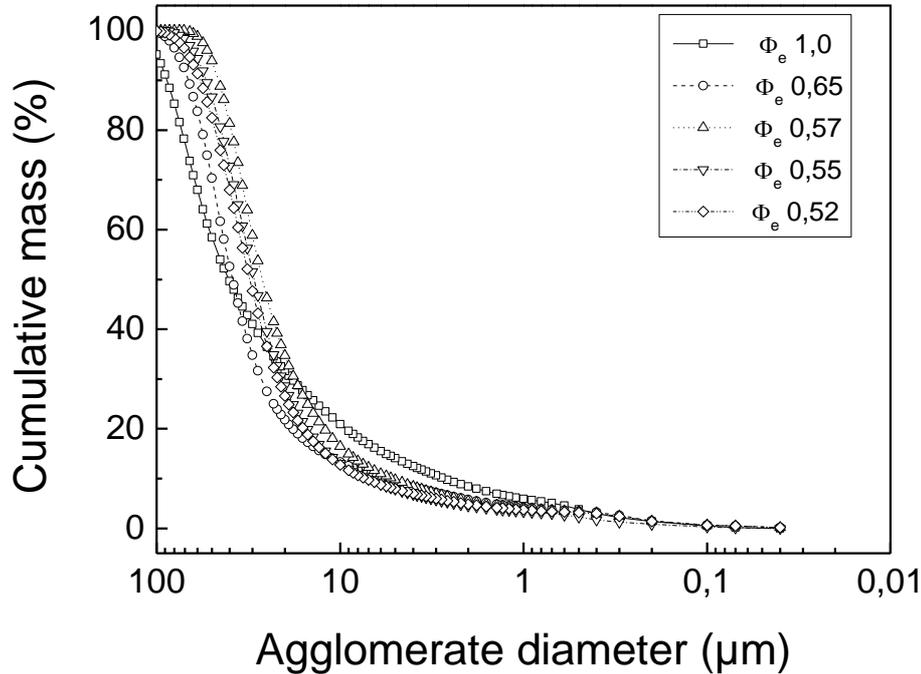


Fig. 3 – Cumulative size distributions of synthesized and milled NiO-YSZ powder

Table 2 shows the density and porosity of the sample NYSZ 2.75 sintered in air at 1450°C for 1 hour. Literature indicates that the appropriate porosity level of Ni-YSZ cermet for anode application is around 40%. In addition, during the reduction process, the initial NiO volume is reduced by 41.1%, generating pores [9]. In the studied material the total porosity will be the 21.9% from NiO reduction plus 27.6% of the porosity obtained during sintering process. The expected total porosity is 48.5%. In this context the relative density and open porosity is appropriate to obtain the percolation porous phase after reduction.

Table 2 Apparent density and porosity of sintered sample NYSZ 2.75 ($\Phi_e = 0.55$)

Sample	Apparent density [g/cm ³]	Apparent density [% pt]	Porosity [%]
NYZ-275	4.42	68.8	27.6

Fig. 4 shows the microstructure of NiO-YSZ composite sintered at 1450°C for 1 hour. The micrographs reveals high porosity of sample. From Fig. 3(b) it can be seen that the average grain size of YSZ and NiO were less than 1 μm and that the distribution of NiO grains in YSZ matrix is random and homogeneous.

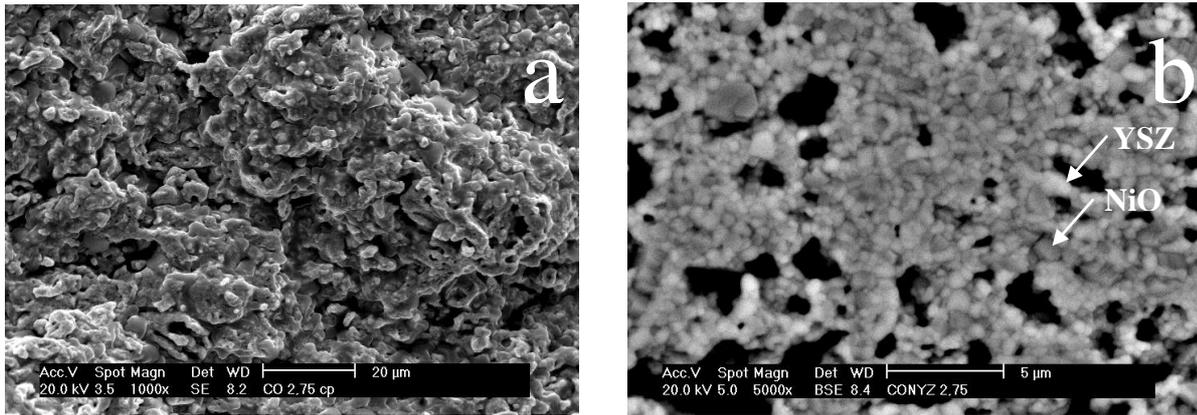


Fig. 4 - SEM micrographs of NiO-YSZ sintered sample NYSZ 2.75 ($\Phi_e = 0.55$):
(a) fractured

Conclusions

Solution combustion synthesis based on urea-nitrate combustion has been developed to obtain nanocrystalline NiO-YSZ powder. When the ratio of fuel to nitrates was stoichiometric and twofold the stoichiometry, the final products were amorphous and have a higher surface area. A fuel-rich solution leads to the formation of crystalline powders. The morphology of the as-burnt powders were nonuniform shaped with large aggregates and irregular foamy aspect. The surface area decrease with the increasing reaction temperature. Such behaviour may be attributed to the aggregation and sintering of small particles.

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