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Ceria-based electrolytes prepared by solution combustion synthesis: The role of fuel on the materials properties

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ABSTRACT

$Ce_{0.8}Sm_{0.2}O_{2-x}$ powders were synthesized by solution combustion synthesis using citric acid, cellulose and sucrose as single, or intimately mixed, fuels. The powders were characterized by X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, N_2 sorption at −196 °C, H_2-temperature programmed reduction and thermogravimetric analyses. Textural properties of the powders were shaped by the peculiar employed fuel. The study of reducibility revealed that oxygen vacancies formation is mainly influenced by both parameters, specific surface area and total pore volume. The different tendency toward reduction played a key role in sintering under reducing atmosphere (4% H_2/Ar), and $Ce_{0.8}Sm_{0.2}O_{2-x}$ prepared with sucrose showed, at scanning electron microscopy images, the highest average grain size. Impedance spectroscopy experiments in air disclosed different grain boundary resistances on the basis of synthesis fuel employed and, in particular, $Ce_{0.8}Sm_{0.2}O_{2-x}$ prepared with sucrose exhibited the best electrical performance. Solution combustion synthesis thereby was able to tailor the morphological and reduction properties of $Ce_{0.8}Sm_{0.2}O_{2-x}$ powders affecting even the microstructure of sintered pellet.

1. Introduction

Nowadays, the research on electrolytes for solid oxide fuel cells (SOFCs) is voted to the development of materials able to enhance the electrical efficiency in the intermediate temperature range (IT-), *ca.* 500–800 °C. Due to the high ionic conductivity below 900 °C, lanthanides doped cerium oxides ($Ce_{1-y}Ln_yO_{2-x}$) represent the most reliable candidates for a large scale technological development of SOFC devices [1–4]. Doping of CeO_2 with a trivalent rare earth element introduces, for charge compensation, an opportune amount of oxygen vacancies ($V_O^{\bullet\bullet}$) that allow charge transport by drift through oxide matrix. However, at the dopant concentration of about 10–20%, necessary to achieve a suitable ionic conductivity, the formation of stable complexes $Ln - V_o^{\bullet\bullet}$ might block the oxygen vacancies and hinder the ionic transport. For dopant content besides 20 at.% the ionic conductivity is strongly blocked. According to the literature, samarium – just followed by gadolinium – is the most promising dopant, not only due to its proper ionic radius, but also to a lower tendency to form $Sm - V_o^{\bullet\bullet}$ complexes [3,5,6]. However, the accurate selection of type and content of dopant is not sufficient to ensure suitable electrical performance, because at the grain boundaries accumulation of $V_O^{\bullet\bullet}$ and Sm(III) might hinder the conductivity. As the grain boundary resistance represents the limiting factor for the overall electrical performance, the fine texture of the electrolyte material is of paramount importance [7–10]. In this respect, firstly a full density material (90–97%) is required for enhancing the ionic transport and, secondly, alio-dopant and impurities segregation to the grain boundaries must be minimized. Actually, special attention has been paid to sintering mechanism of doped ceria and it is, on the whole, established that grain growth is promoted by surface and grain boundary diffusions at the early stages of sintering, whereas at high temperature lattice diffusion mechanism activates densification and exclusion of pores. However, segregation phenomena to the grain boundaries interfere with diffusion process limiting the coarsening of particles [11–13]. Consequently, suitable particle size and porosity of powders used for membrane fabrication are pivotal for the microstructure and density of the final material. To design doped ceria as electrolyte it is mandatory to define peculiar sintering procedures and synthesis method for shaping the starting powders and achieving effec-

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tive electrolytic membranes. For instance, Esposito *et* al. referred that employing nanostructured Sm- or Gd-doped (20 at.%) ceria, as starting powders for fast firing sintering, allows to reduce the grain boundary contribution to the to total conductivity. Thanks to high surface energy of small sized particles and to short sintering time, full density materials have been obtained with low grain growth and limited segregation phenomena [11]. Esposito et al. successively explored the sintering of $Ce_{0.9}Gd_{0.1}O_{2-x}$, (CGO), both with high and low specific surface area, in 9% H_2/N_2 with the purpose of forming an opportune amount of oxygen vacancies on the surface of particles for favouring the densification. Authors noted that high densification was reached at lower temperatures compared to conventional temperatures reached in air. Furthermore electrical conductivity of CGO sintered under 9% H_2/N_2 was competitive with the value extrapolated for CGO conventionally sintered [12]. More recently, Ni *et* al. investigated the effects of slurry-based techniques for shaping the porosity of CGO powders. They verified that pore sizes affect grain growth and, in particular, small pores were determinant for densification at the initial stage of sintering, whereas large pores influenced the sintering process at high temperature [13]. Several papers dealt with methods able to produce porous material with controlled grain size, in most of them the use of auxiliary substances is reported [14–16]. On the other hand, the use of additives renders more cumbersome the overall membrane fabrication procedure and may have a negative impact on the total conductivity. Almost always, it is possible to bypass these aided methods selecting a suitable synthesis method: in this light, solution combustion synthesis (SCS) represents a flexible method to produce, by single step, nanostructured and ultra-fine powders with suitable microstructural properties [17–23]. According to the method, the synthesis fuel has the triple role of: (i) propellant, (ii) complexing agent, (iii) microstructural template. Playing with the fuel, it is possible to modulate the microstructure of powder and to create an adequate porous network which represents a fundamental starting point for the densification process [24–27].

The present work aims to evaluate the effect of SCS on morphological properties of $Ce_{0.8}Sm_{0.2}O_{2-x}$ powders and to assess the impact of sintering under 4% H_2/Ar on the electrical properties of the final products. In this respect, three different fuel of synthesis were selected: citric acid, cellulose-citric acid and sucrose. The powders were characterized by XRD, XPS, TEM and N_2 adsorption at −196 °C. Moreover, H_2-TPR and TGA analyses were carried out in order to evaluate the presence of surface oxygen vacancies and as well the capacity of powders to create oxygen vacancies at high temperature under reducing atmosphere with a view to correlate reduction features with microstructure after sintering under hydrogen atmosphere. Special efforts were brought in relating powder and sintered material microstructure with electrical performance.

2. Experimental

2.1. Materials preparation

$Ce_{0.8}Sm_{0.2}O_{2-x}$ powders were prepared by solution combustion synthesis using $Ce(NO_3)_3 \cdot 6H_2O$ (99.99% Sigma-Aldrich) and $Sm(NO_3)_3 \cdot 6H_2O$ (99.99% Sigma-Aldrich) as metal precursors and as combustion fuel mixtures: 1) citric acid ($C_6H_5O_7$ anhydrous, ≥99.5% Sigma-Aldrich) with ammonia (28 vol.% NH_3 in H_2O, ≥99,99% Sigma-Aldrich); 2) cellulose (powder with degree of substitution zero, DS-0, for thin layer chromatography, Fluka Analytical) and citric acid in the 2:1 molar ratio; 3) sucrose (Eridania Italia Spa ©). According to propellants chemistry [28], the combustion reactions were carried out in stoichiometric condition (Φ = reducers-to-oxidizers molar ratio = 1) with a fuel-to-metal cations molar ratio set to 2. To achieve this purpose, a proper amount of ammonium nitrate (NH_4NO_3, ≥99,0% Sigma-Aldrich) was added to reaction mixtures as oxidant regulator for fixing Φ equal to 1. Metal nitrates, fuel and additives were dissolved in aqueous solution in a stainless steel beaker. The reducers-oxidizers mixture was stirred at 80 °C until a pale gel was formed. By increasing the temperature, a white dendritic powder was formed for all combustion reactions, and then fired in air for 5 h at 1000 °C. Samples were referred to with SDC-1, SDC-2 and SDC-3 abbreviations indicating the $Ce_{0.8}Sm_{0.2}O_{2-x}$ powder composition as SDC and the combustion fuel mixtures as: 1 for citric acid and ammonia; 2 for cellulose and citric acid; 3 for sucrose. The above synthesized powders were isostatically pressed at 200 MPa and treated at 1400 °C for 4 h in H_2/Ar (4vol%) for registering impedance spectroscopy analyses (see below). The final pellets had a diameter of about 7.8 mm, a thickness of about 3 mm and a density encompassed between 94 and 97% of theoretical value. The final densities were determined using the Archimedes method.

2.2. Materials characterization

X-ray diffraction (XRD) measurements were collected with a Siemens D5005 X-ray powder diffractometer equipped with a curved graphite monochromator on the diffracted beam. The observed range 25–90° 2θ was scanned with a step size of 0.02° 2θ and an integration time of 3s *per* step. Rietveld refinement of the diffraction patterns was carried out by using the GSAS package [29]. Chebyscev polynomials and Pearson VII functions were chosen for the background and for the peak profile fitting, respectively. In the structure refinement lattice constants, atomic coordinates, scale factors and full width at half maximum (FWHM) parameters were considered as variables. The estimation of the crystal size values was obtained from Scherrer equation, in agreement with the GSAS package procedure.

The X-ray photoelectron spectroscopy analyses were performed with a VG-Microtech ESCA 3000Multilab, equipped with a dual Mg/Al anode. The spectra were excited by the unmonochromatized Al Kα source (1486.6 eV) run at 14 kV and 15 mA. Since Ce(IV) could easily undergo photo-reduction, measurements were carried out with short irradiation scans in the region of Ce 3*d* and long irradiation times for the other elements. The Ce 3*d* region was recorded as soon as the sample was put under the X-Ray and afterwards all the other regions were recorded. This allowed a very low irradiation time but gave a poor signal-to-noise ratio. The analyser operated in the constant analyser energy (CAE) mode. For the individual peak energy regions, a pass energy of 20 eV set across the hemispheres was used. Survey spectra were measured at 50 eV pass energy. The sample powders were analyzed as powder, mounted on a double-sided adhesive tape. The pressure in the analysis chamber was in the range of 10^{-8} Torr during data collection. The invariance of the peak shapes and widths at the beginning and at the end of the analyses ensured absence of differential charging. Analyses of the peaks were performed with the software provided by VG, based on non-linear least squares fitting program using a weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley and Sherwood [30,31]. Atomic concentrations were calculated from peak intensity using the sensitivity factors provided with the software. The binding energy values are quoted with a precision of ±0.15 eV and the atomic percentage with a precision of ±10%.

Specific surface area (BET method) [32] and pore size distributions (BJH method) [33] were evaluated performing nitrogen adsorption/desorption measurements at −196 °C, using a Sorptomatic 1900Carlo Erba equipment. All the samples were pretreated under vacuum at 250 °C for 2 h prior to the measurements.