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FUEL CELLS AND NANOPARTICLES

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ABSTRACT. Many new chemical methods are being developed and existing ones modified in order to improve the particles produced and the cost-effectiveness of the process. In our project, yttria stabilized zirconia (YSZ) nanoparticles with a mean particle diameter between 7 and 10 nm have been obtained using a calcination temperature of only 500^{o}C through a modified sol-gel method using two new organic precursors: sucrose and pectin. These precursors are a good solution to the disadvantages presented for the sol-gel method, being cost-effective, ubiquitous and environmentally friendly. The calcination process was studied by thermal analysis (TA) and the crystal structure is analyzed by XRD The particle size was determined by Transmission Electron Microscopy (TEM), supported by the X-ray Diffraction (XRD) determination of the crystallite size using the Scherrer formula, and the Brunauer, Emmet, and Teller (BET) adsorption analysis used to determine the specific surface area.

INTRODUCTION

As reserves for the common fossil fuels become smaller and their use lead to important pollution, alternative energy sources and processes are increasingly the focus of research and development. Fuel cells are electrochemical cells that generate electricity through the oxidation of hydrogen or another gaseous fuel (rich in hydrogen), mostly using oxygen from the air. [1-3].

The materials that constitute the electrolyte and the electrodes determine the type of the fuel cell [4]. In SOFCs, all three components are made from ceramic materials. SOFCs are distinguished from other fuel cell types by: the solid electrolyte; the highest working temperature; a high efficiency; simplicity and their ability to generate electricity directly from

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hydrocarbon fuels, meaning that, for instance, all of hydrogen (H2), carbon monoxide (CO) and methane (CH4) can be used as fuels, the second one being a poison when used in most other types of fuel cell [2, 5].

The solid electrolyte is an oxidic material, most often yttrium stabilized zirconia (YSZ) [6]. Adding a small percentage of Y_2O_3 to ZrO_2 has two effects: i) it stabilizes the cubic structure of zirconium oxide at all temperatures and ii) substituting some tetravalent zirconium ions with trivalent yttrium ions gives rise to oxygen ion vacancies in the crystal structure. [7].

The YSZ electrolyte must be dense, i. e. free of porosity, it must possess high oxygen ion conductivity and a minimal electronic conductivity, it must have high mechanical strength, good chemical stability and durability and it must be compatible with the other components (the electrodes) in terms of thermal expansion. [7, 9-11].

The working principle of a fuel cell is depicted in Figure 1. As gaseous oxygen is fed into the porous cathode, the molecules are split on the cathodic catalyst, which consumes electrons, and O2¡ ions pass into the electrolyte. The electrolyte conducts these ions through oxygen vacancies toward the anode. Here these ions, together with hydrogen from a fuel, form water, which releases electrons. These electrons are conducted through the anode material and captured by a current collector behind the anode and further through an external circuit and a cathodic current collector to the cathode, where they are again consumed in the cathodic process [1-3, 7, 8].

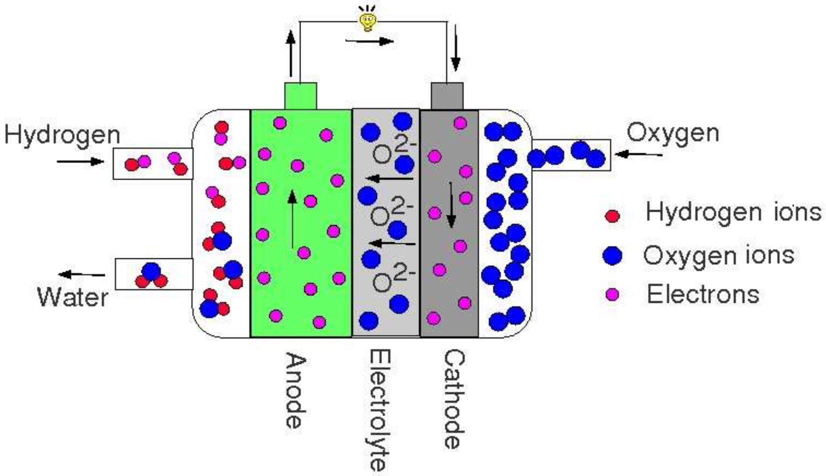

Figure 1. SOFC principle. The electrodes are porous, so that the gaseous molecules actually penetrate right down to the electrolyte

As mentioned, SOFCs use a catalyst (metallic, usually nickel) on one or both electrodes to increase the rate of a reaction without being consumed in the processes [7, 8]. The electrochemical reactions involve gaseous reactants and/or products, ionic reactants and/or products and electrons. The electrochemically active region therefore needs to be accessible to all three of these species, and is thus on the interface between the pores transporting the gaseous reactants/products, the electrolyte conducting the ions, and the catalyst in the electrode conducting electrons. This interface represents the \triple-phase boundary" (TPB) and the efficiency of the electrochemical reactions of the cell depend on its extent (see Figure 2) [12-17].

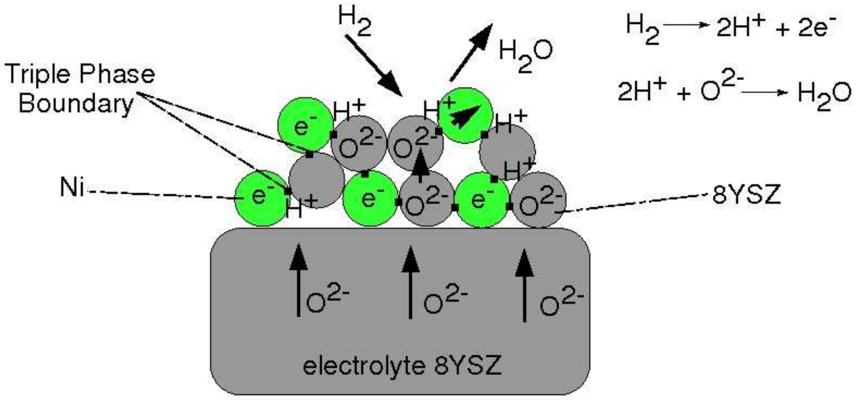

Figure 2. SOFC triple-phase-boundary (TPB). Often, as also depicted in this figure, particles of electrolyte material penetrate into the electrode, increasing the TPB

Our research project is focused on producing nano-sized powders for use as precursors for manufacture of SOFC components. In the manufacture, using nanoparticles gives rise a decrease in the required temperature of sintering, an improvement in the homogeneity of the produced films, a more homogeneous distribution of the doping elements, increased homogeneity of the microstress distribution, enhanced mechanical properties under temperature change and enhanced gas passage through the electrodes [18].

There are a multitude of different processes to produce nanoscaled materials today. These are usually classified into *physical methods* (e. g. plasma spraying [19, 20], flame synthesis [21, 22], electrostatic atomization [23], microwave flash synthesis [24], *chemical methods* (e. g. sol-gel [25-27], precipitation [28-30]) and mixed *chemical-physical methods* (e. g. spray pyrolysis [31, 32], flame-spray synthesis [33]).

Concentrating on chemical methods used for producing zirconia-based nanoparticles, present common advantages such as low costs, good control of stoichiometry, good mixing of the starting materials and good chemical homogeneity of the product. On the other hand, particle agglomeration and costly chemical precursors are a few disadvantages of this type of method.

In this paper, we focused on obtaining ultra fine zirconia powders. Traditional organic precursors for the sol-gel process have been replaced with sucrose and pectin, an alternative which has not been tried out before. The aim was to synthesize the powder and characterize it using thermal analysis, transmission electron microscopy, scanning electron microscopy, X-ray diffraction, and BET analysis.

EXPERIMENTAL

The common salts $ZrCl_4$ (Sigma-Aldrich, technical purity) and $Y(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich, 99. 9% purity) were used as zirconia and yttria precursors, respectively. The process followed the floe chart presented in Figure 3. Zirconium chlorate was dissolved in distilled water on a warming plate at 100°C. Next, the yttrium nitrate for a final composition of 8mol% Y_2O_3 to ZrO_2 were calculated, weighed and added to the solution. After the homogenization, a sucrose / pectin mixture with a mass ratio of 4:0. 1 was added to the solution under continuous stirring and the pH of the final solution is between 0. 5–1.

The aim of the stirring under heating treatment is to maintain the degree of dispersion on an advanced scale, to prevent agglomeration of the constituent particles and to avoid their solidification into crystals. The thermal treatment continues and the mixture is dried at 90–100°C and is allowed to stand for 2h. During this, from the clear solution the sol and the gel are gradually formed. The thermal treatment is mainted for another 2-3h until the mixture becomes completely gelatinized and the dried gel (xerogel) is formed. The xerogel is then subjected to a calcinations thermal treatment in order to be transformed into YSZ nanoparticles. The thermal treatment used for the samples at 500°C has a 6h plateau at the maximum temperature at a heating/cooling rate of 100°C/h. The samples obtained at 1000°C the thermal treatment has 1h plateau at the maximum temperature at a heating/cooling rate of 100°C/h.

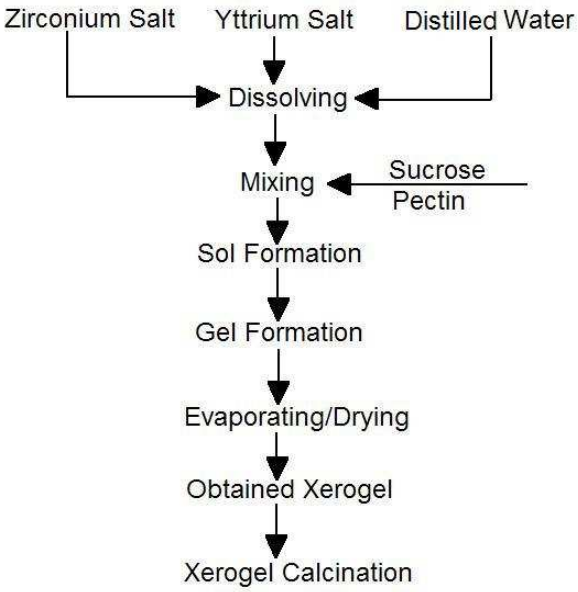

Figure 3. The flowing chart for the YSZ nanoparticles preparation

RESULTS AND DISCUSSIONS

The evolutions of the dried gel was recorded by *Thermal Analysis (TA)* using a Derivatograph Q 1500 (MOM Hungary) based on the F. Pauli, J. Pauli and L. Erdey principle. Small samples of dried gel were taken from the sample was analyzed as a function of temperature at a heating rate of 10°C/min. The TA results are shown in Figure 4.

The DTA curve has shown a strong exothermic process which is starting at 280-300°C and continues up to 850°C. The inflexion points observed at 450°C and between 650°C and 850°C attributed to oxidation of the organic compounds, ZrO_2 formation, and the formation of solid solution between ZrO_2 and Y_2O_3. Because the processes are overlapped it is difficult to limit the intervals attributed to each process.

The TG curve shows a process with little mass losses at the temperature of 100°C due to the water elimination, followed by a higher mass loss at 300°C and a slower mass loss up to 700°C. The total losses were 56%.

After passing the temperature of 850°C no processes can be observed either on the mass variation curves TG or on the DTA curve.

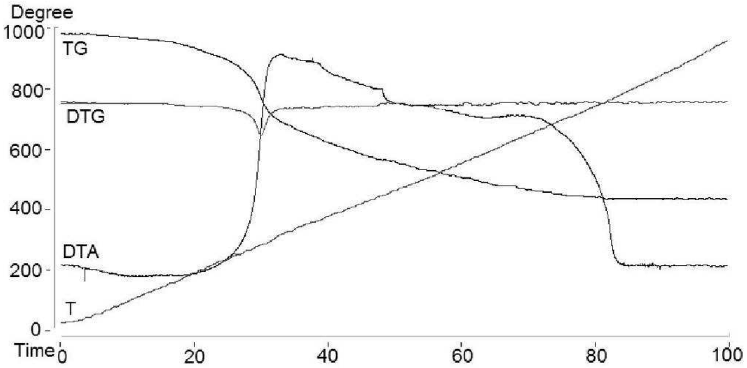

Figure 4. TA analysis of the YSZ gel

The X-ray diffraction spectra were obtained by Brucker D-8 Advance X-ray diffractometer using a Cu K-α radiation. The unit cell parameter accuracy was ±10^{-3}Å. The intensities were measured from 20 to 100° with a counting rate of 3 s per scanning step. The obtained spectra showed that the obtained nanoparticles at temperatures of 500 and 1000°C are stabilized in cubic crystal form (see Figure 5). The presence of other was not observed.

The Scherrer formula applied on the first four peaks of the obtained XRD spectrum was used in order to determine the crystallite size of the particles. The Cukα1 radiation value used for determination was 0. 15406 nm and the k value equal with 1. The crystallites size increase with increasing the temperature from 7 nm at 500°C to 33 nm at 1000°C.

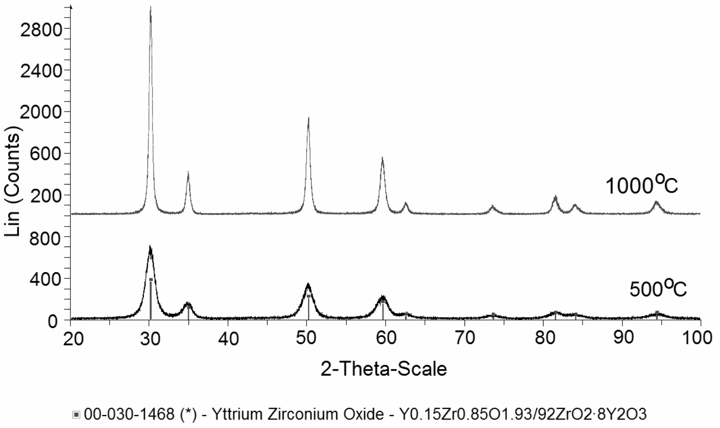

Figure 5. XRD spectra of the YSZ samples at 500 and 1000°C

The specific surface area was determined from *nitrogen adsorption* using a Gemini 2380 from Micromeritics. The samples were degassed at 300°C for 3 hours under vacuum before analysis. At 500°C high singlepoint and multipoint BET values were obtained corresponding to 80 m^2/g and 83m^2/g, respectively. At 1000°C the singlepoint and multipoint values decrease to 8. 2 m^2/g and 8. 6 m^2/g, respectively. The particle size was calculated assuming that the particles are round and that the density of the cubic ZrO_2 is 5900 kg/m^3. In this way, particle of 12 nm are obtained at 500°C and around 120 nm at 1000°C. In agreement with the XRD data, the BET values show that the smallest particle sizes are obtained at low temperatures while increasing the temperature the particle size also increases.

Figure 6 shows the *transmission microscope* images of the obtained YSZ particles. The images were obtained using a JEOL-JEM-1011 transmission microscope. The used copper grids during TEM investigations were subjected to a carbon deposition followed by a glow discharge. In the meantime, the powders were dispersed in distilled water under stirring and one drop taken from the solution was deposited on the prepared copper grid.

The morphology of all samples has shown relatively uniform and round shapes with a narrow size distribution. Particles around 8 nm are obtained at 500°C and around 55 nm at 1000°C. For the particles obtained at 500°C can easily be seen that the individual particles are easy to distinguish, and are not agglomerated to a very large degree in contrast to the particle obtained at 1000°C. At the highest temperature the particle very easily form agglomerates and the particles are difficult to distinguish.

In figure 7 *scanning microscope* picture of the sample obtained at 1000°C is presented. Large agglomerates with the mean particle size around 53 nm are obtained.

CONCLUSIONS

It is possible to produce YSZ nanoparticles in relatively simple conditions and at low costs. The new organic precursors (sucrose and pectin) are cheap, non-toxic, available at industrial scale, easy to store and manipulate at low temperatures. The method is environmentally friendly since it is water based and uses two natural compounds as organic precursors.

The results have shown that the new sol-gel method can be easily use to obtain nanoscaled powders for the sintering of YSZ ceramics with the aim of manufacturing SOFC electrolytes or anodes.

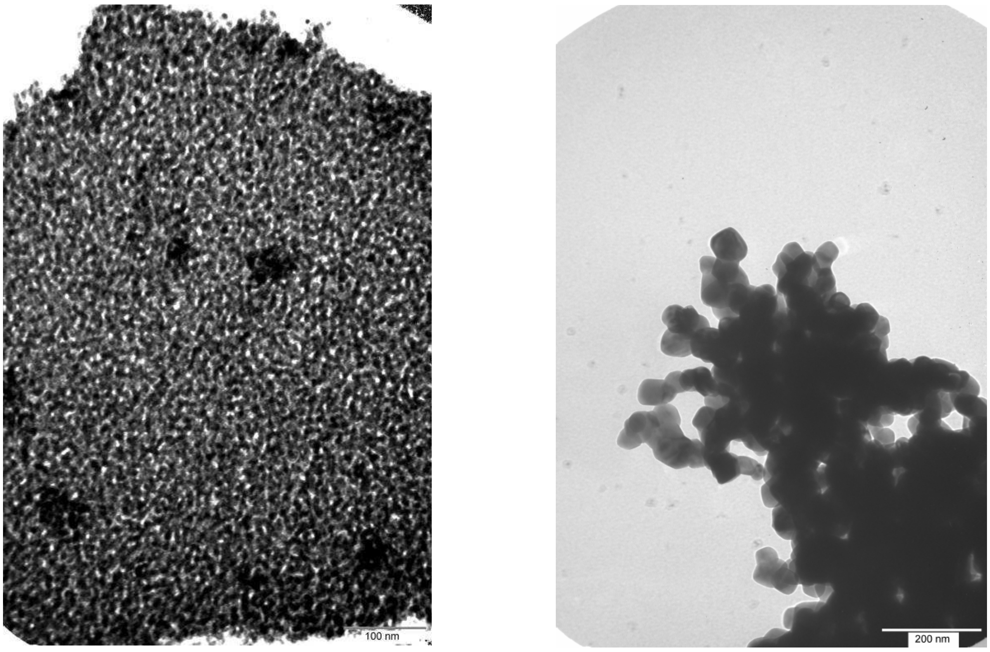

Figure 6. TEM pictures of YSZ obtained at 500 and 1000°C

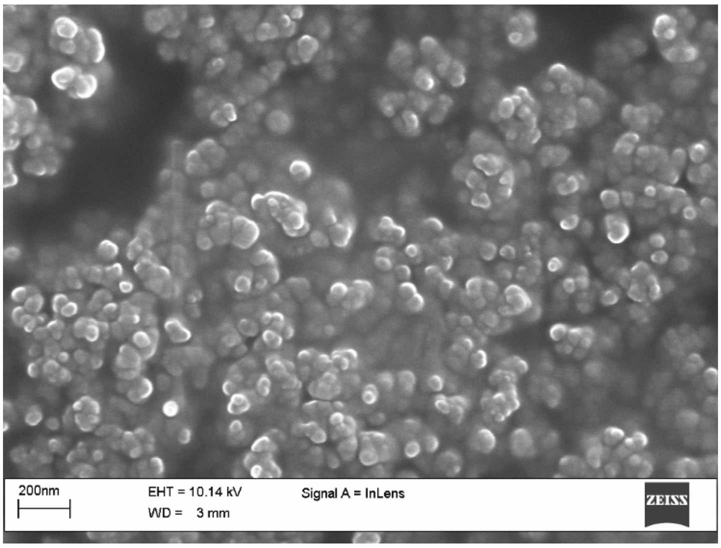

Figure 7. SEM image of the YSZ samples obtained at 1000°C

The XRD analysis gives the measure of the crystallite itself as components of the particle. Thus, the crystallite sizes calculated from the XRD analysis with the Sherrer formula are little less than the particle sizes measured using TEM analysis. The TEM analysis seems to be the most reliable method to determine the particle size because this is directly measured and, in addition, it give information about the shape and the morphology of the powders. The larger particle size determined by the nitrogen adsorption analysis can be affected by errors due to the particle agglomeration especially at high temperatures where the particle adhere to each other.

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