NANOMATERIALS FOR SOFC ELECTROLYTES AND ANODES ON THE BASE OF ZIRCONIA

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ABSTRACT

Weakly agglomerated ZrO₂ nanopowders were stabilized by 3% and 8% Y₂O₃ and obtained by co-precipitation using microwave (MW) heating, exposure to impulse magnetic field, and ultrasonic treatment. While obtaining stabilized zirconia, the processes of dehydration and dehydroxilation (the release of OH groups) were studied by means of electron microscopy, X-ray structure analysis, and NMR. It is shown that MW and impulse magnetic field treatment combined with ultrasonic influence provide high specific surface of the hydroxide. The particle size of the powders can be controlled with the help of these effects and thermal processing. In the present work, this size ranges from 9 to 18 nm for tetragonal zirconia and reaches 5 to 6 nm for cubic zirconia. It is shown that the use of obtained nanopowders makes it possible to reach high structural homogeneity for ceramics as well as for the composite (with Ni) samples.

INTRODUCTION

The main issues in SOFC development are the increase in ion conductivity of the electrolyte, the reduction of the operation temperature, longer lifetime, thermal cyclability, and the enhancement of chemical robustness (1). SOFCs produced at present are very costly, and materials may amount to 50% of the total cost. Despite significant progress, these materials do not meet all the requirements for a cost-effective SOFC.

Recent investigations have shown that needed changes in physical and mechanical properties of materials can be achieved by the creation of powder-based nanoscale structures. The most appropriate compound is zirconia, which is the starting material for two of three main components of the majority of SOFCs, the high-density ceramic electrolyte and the metal-ceramic (with Ni) porous anode. It is also a constituent of composite porous cathode, a cathode based on LaₓSrₓMnO₃. Nanopowders provide a number of advantages for SOFCs:

- increase in ion conductivity of the electrolyte
- enhancement of the catalytic capacity of the cathode and anode
- reduction of polarization losses at the cathode-electrolyte interface
- decrease in the temperature of sintering
- homogeneity of distribution of doping elements
- increased homogeneity of micro-stress distribution and enhanced mechanical properties at temperature change and gas passage through electrodes
- possibility of formation of very homogeneous films (10-15 μm).

Some of these merits have already been demonstrated in the context of SOFC issues. It is shown in (2) that nanocrystal tetragonal ZrO$_2$+ 4 mol% Y$_2$O$_3$ has higher conductivity than cubic ZrO$_2$ + 9.5 mol% Y$_2$O$_3$ with large crystals.

The high cost of nanopowders today is due to the fact that complex low-volume production processes with high energy consumption are used to obtain nanopowder materials of high purity, characterized by small deviation of particle size and a low level of aggregation and agglomeration of the particles. These methods are condensation from the vapor phase, chemical and electrochemical precipitation, plasma evaporation of a solid phase, and laser synthesis of a liquid precursor. Additional doping with Ce, Sc, and rare-earth materials increases the difficulty of obtaining materials and increases their cost for SOFC components. A well-known method of coprecipitation does not provide the required properties.

This paper depicts experimental results of tests to improve the coprecipitation method by using the physical effects of ultrasound (US), impulse magnetic field (IMF), and microwave (MW) heating partially depicted in (3). The main aim of the work is to obtain nano-dispersed, weakly aggregated powders of tetragonal ZrO$_2$ + 3 mol% Y$_2$O$_3$ from cubic ZrO$_2$ + 8 mol% Y$_2$O$_3$ using inexpensive Ukrainian raw materials. These compositions were chosen to obtain optimal characteristics of conductivity of cubic zirconia and mechanical properties of the tetragonal phase.

The processes taking place during the heating of products of coprecipitation have been studied as has the influence of US, IMF, and MW on the formation of zirconia. The possibility of obtaining ceramic composite samples based on ZrO$_2$ with addition of Ni is also presented.

METHODS OF OBTAINING AND INVESTIGATING POWDERS

ZrO$_2$-3 mol% Y$_2$O$_3$ powders were obtained by inverse coprecipitation of hydroxides from nitrate solutions by means of hydrous solution of ammonia at pH 9. The precipitate was washed several times to remove byproducts of the reaction.

The hydrogel was dried at 120°C. The furnace with parameters of 600 W capacity and 2450 MHz frequency was used for MW treatment of hydroxides. The powders were dried in IMF at 120°C in a special setup with the magnetic field strength of $H = 10^4$-10$^5$A/m and frequency $f = 0.5$–10 Hz. The zirconia powders were treated with US at cavitation in a US chamber (capacity 400 W, cell volume 1000 cm$^3$, frequency 22 kHz) and using a US generator (capacity 10 kW, volume of container 350 cm$^3$). The calcination was in the range 400–700°C. The measurement of specific surfaces of dry hydroxides and produced oxides was carried out by BET. The phase composition and size of the X-ray coherent scattering area (CSA) of powders and ceramics were studied by X-ray analysis; the structure of powders and ceramics was examined by transmission and scanning electron microscope (TEM and SEM).
A thermogravimetric setup was developed to study the process of dehydration, which allowed us to estimate the mass loss from heating zirconia within the MW furnace, IMF setup, and the thermo-box (4). The process of dehydroxilation (the release of OH groups) was studied by NMR with protons (^1H) at a frequency of 20 MHz and magnetic induction 0.47 Tl.

**EXPERIMENTAL RESULTS**

While producing nanopowders, a dispersed system is changed. Thin amorphous plates of significant size (~5–200 µm) are formed as a result of drying the products of coprecipitation (Figure 1a). The heating evokes dehydroxilation (loss of OH groups), and at 400°C crystallization occurs. The plates are destroyed and rather large planar particles are formed (0.3-1 µm) if no special method is used. Crystal growth is observed at temperatures above 400°C, and partial sintering occurs at higher temperatures (>700°C).

![Figure 1. SEM image of amorphous product of coprecipitation of Zr and Y oxynitrates: a) after drying at 120°C without special effects; b) with MW heating.](image)

The kinetics of dehydration of hydrous precipitate of zirconia-yttria hydroxide within the drying box (curve 1), in the MW furnace (curve 2), and in IMF at 120°C (curve 3) is presented in Figure 2. These results show that MW drying of zirconia dioxide causes an increase in the rate of dehydration equal to 0.2%/min in the case of convection drying and 1.6%/min for MW drying of an equal quantity of material. The increased rate of liquid release is responsible for forming a looser structure of the hydroxide (Figure 1b). The rate of drying rises less significantly (0.8%/min, see curve 3 on Figure 3) with IMF use than with MW heating. The influence of IMF on the drying of zirconia was studied (5) and showed that IMF raises the activity of thermal decomposition of zirconia manifested as dehydration and dehydroxilation (release of OH groups) and decreases the level of agglomeration of the powder at the rate of enhancement of its dispersion. The beginning of crystallization appears to be shifted toward lower temperatures. Our last NMR study allowed examination of the dehydroxilation process of the powders obtained with
Figure 2. The kinetics of drying of zirconium hydroxide: 1) at 120°C; 2) in MW field; 3) in IMF field at 120°C.

Figure 3. NMR $^1$H spectrum of ZrO$_2$-8 mol% Y$_2$O$_3$ powders calcinated at 500°C; 1) experimental curve; 2) Gauss and Lorentz fitting curves of the derivative of absorption line.

with physical effects. It has been found that at least two lines (wide and narrow) can be separated from the NMR proton spectrum of samples after heating at 500°C (see Figure 3).

As far as preliminary heating at 120°C removes physically bound water, the presence of two lines can be conditioned just by protons of hydroxyl groups OH in two different states. The temperature dependence of both the wide and narrow line width is indicative of the presence of finer distribution of bond types of protons and OH groups (Table 1). The effects of different types of drying are explicitly seen while analyzing the change of specific surface (Table 2).
Table 1. NMR $^1$H Data of ZrO$_2$-8 mol% Y$_2$O$_3$ Powders at Different Temperatures.

| T, °C | Wide line | Narrow line |
|------|-----------|-------------|
|      | Area      | Width       | Height      | Area      | Width | Height |
| 120  | 0.62      | 6.32        | 0.059       | 4.9       | 0.70  | 2.397  |
| 400  | 0.2       | 3.4         | 0.36        | 0.2       | 0.79  | 0.106  |
| 500  | 0.58      | 3.09        | 0.13        | 0.        | 0.5   | 0.14   |

Table 2. Dependence of Specific Surface of ZrO$_2$ + 3 mol% Y$_2$O$_3$ from the Treatment and Temperature.

| Temperature of heating, °C | Specific surface $S_{\text{BET}}$, m$^2$/g |
|----------------------------|-------------------------------------------|
| 120°C                      | 200                                       |
| MW                         | 270                                       |
| IMF                        | 300                                       |
| 120°C+US                   | 295                                       |
| MW+US                      | 395                                       |
| IMF+US                     | 387                                       |
| 400                        | 130                                       |
| 500                        | 103                                       |
| 600                        | 75                                        |
| 700                        | 33                                        |
| 134                        | 89                                        |
| 180                        | 130                                       |
| 139                        | 94                                        |
| 139                        | 107                                       |
| 145                        | 114                                       |
| 130                        | 80                                        |
| 139                        | 67                                        |
| 139                        | 73                                        |
| 145                        | 78                                        |
| 180                        | 40                                        |
| 107                        | 40                                        |
| 114                        | 45                                        |
| 78                         | 55                                        |

It is well known that partial sintering of nanopowder particles above 700°C is responsible for the formation of rigid aggregates and agglomerates that significantly reduce the merits of nanopowders (6). The use of US treatment combined with the traditional drying, MW and IMF drying, results in the increase of the specific surface of the zirconium hydroxide up to 300 and 400 m$^2$/g (7).

The crystallization of oxides occurs at 400°C without a noticeable change in the magnitude of exothermal peak for all the samples. A minor reduction of the area of crystallization peak of samples treated by IMF is in accordance with the EM data concerning partial crystallization of the powder during drying. It should be mentioned that the size of CSA in powders treated by MW and IMF appears to be lower in comparison to the traditional drying at all temperatures of heating (Table 3). Probably, it is associated with the increase in the quantity of crystal nucleus or with proper conditions for its formation during MW and IMF treatment.

Table 3. Dependence of CSA Size of ZrO$_2$ + 3 mol% Y$_2$O$_3$ Powders from Treatment and Temperature of Heating.

| Treatment | Temperature of heating, °C | CSA size, nm |
|-----------|----------------------------|--------------|
|           | 400 | 500 | 700 |
| Initial   | 12.6| 12.1| 17.6|
| MW        | 10.6| 11.9| 15.1|
| IMF       | 9.3 | 10.1| 16.2|
| 120°C+US  | 10.5| 12.5| 18.0|
| MW+US     | 8.9 | 9.9 | 15.9|
| IMF+US    | 8.7 | 10.2| 14.1|

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The results obtained allow us to conclude that at properly chosen conditions of treatment, it is possible to synthesize a weakly agglomerated powder of zirconia (3 mol% and 8 mol% Y₂O₃) characterized by tetragonal modification and narrow distribution of particle size. The powder with CSA size equal to 5–6 nm and the specific surface more than 140 m²/g is presented on Figure 4. The experiments to synthesize cubic modification zirconia powder (8 mol% Y₂O₃) gave similar results. This technology provides a high homogeneity of the distribution of doping elements and significant stability of high-temperature phases (tetragonal for 3 mol% Y₂O₃ and cubic for 8 mol% Y₂O₃).

Ceramics with the following characteristics can be obtained from the ZrO₂ + 3 mol% Y₂O₃ powder after compacting at high hydrostatic pressure and sintering at 1400–1500°C: density equal to 5.9–6.0 g/cm³, grain size of 0.2–0.3 μm, flexure strength of 1000 MPa, and fracture toughness coefficient of 8–9 MPa⋅m¹/². Used for production of SOFC electrolyte, ZrO₂ + 8 mol% Y₂O₃ nanopowders provide good quality ceramic films of 50–100 μm thickness by casting. The investigations proved the high homogeneity of structure of the ceramics obtained from these powders. However 100% density in ceramic films was not reached during these experiments because some optimization of sintering conditions is necessary for nanopowders.

The anode composition was prepared; the material contained 60 wt% cubic ZrO₂ and 40 wt% metallic Ni. The source components, zirconia and nickel oxalate powder were synthesized separately. The cubic ZrO₂ powder matrix containing 8 mol% Y₂O₃ was produced by inverse coprecipitation of zirconium and yttrium nitrates with hydrous ammonia solution dried in the MW furnace. Nickel oxalate was obtained from nickel nitrate and ammonia oxalate. The cubic zirconia powder was mixed with nickel oxalate in an ultrasonic container. The components were used in the amount corresponding to the stochiometry of the final composition. The sintered samples had 4.8 g/cm³ density and 35% porosity. The phase composition of the sintered samples was cubic ZrO₂ + (97% Ni + 3% NiO). The SEM study of fractures shown in Figure 5 shows small grain size and high dispersibility and homogeneity of the distribution of highly dispersed Ni particles in the composite.

Figure 4. TEM image of crystallized powder ZrO₂ − 8% Y₂O₃.
CONCLUSIONS

The present study has indicated that the powders on a base of ZrO$_2$ obtained by co-precipitation using MW, IMF, and US treatment are nanoscale, characterized by narrow distribution of particle size, and weakly agglomerated. They can be used successfully in the production of SOFC electrolyte and anode.

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