Aerosol Deposition as a Promising Technique to Fabricating a Thin-film Solid Electrolyte of Solid Oxide Fuel Cells

S. I. Bredikhin^{a,b}, D. A. Agarkov^{a,b}, E. A. Agarkova^a, I. N. Burmistrov^{a,b}, A. M. Cherkasov^a, V. E. Pukha^c, D. V. Yalovenko^a and N. V. Lyskov^c

^a Laboratory of Spectroscopy of Defect Structures, Institute of Solid State Physics RAS, Chernogolovka, Moscow region 142432, Russia

^b Laboratory of Fuel Cells, Moscow Institute of Physics and Technology, Dolgoprudny, Moscow region 141700, Russia

^c Department of Functional Materials for Chemical Power Sources, Institute of Problems of Chemical Physics, Chernogolovka, Moscow region 142432, Russia

> In present work we developed and tested model anode-supported planar solid oxide fuel cells. We used commercially available 2layered (current-collector and functional) anode supports. Thinfilm electrolyte layer based on 8 mol.% yttria-stabilized zirconia (YSZ) was produced by aerosol deposition method using converging-diverging (de Laval) type nozzle. To provide the fabrication of pinhole-free gas-tight thin-film electrolyte coatings, the pre-treatment procedure of initial powders was developed. The optimal operating parameters of the deposition modes of the YSZ solid electrolyte of different thicknesses are determined. Morphology analysis of the obtained thin-film coatings showed that the application of these modes provides the fabrication of thinfilm YSZ layer with thickness of a few microns possessed good adhesion to the anode support, gas tightness and uniformity thickness.

Introduction

Solid oxide fuel cells (SOFCs) are among the most promising technologies for electricity and heat generation in terms of decentralized energy (1-3). Despite of this, SOFCs have quite limited role in a world market of power generators. The main task of research and development teams is to reduce cost and optimize the performance of the technology. Up to half of the complex resistance of planar electrolyte-supported SOFC is associated with solid electrolyte membrane, and this value cannot be decreased significantly due to requirements to mechanical strength of the support element. The more promising types of planar solid oxide fuel cells (SOFC) based on the electrode or outer mechanical support require the use of thin-film deposition techniques to form the electrolyte layer. Decrease of electrolytes' thickness leads to decrease of their impedance and growth of the power density obtained from the SOFC and stack. Productive and cost effective technique for thin-film gas-tight solid electrolyte membrane deposition is a key element of effective SOFC production. Cheap and technological techniques with the origin from the field of microelectronics (e.g. screen print, tape-casting etc.) do not give opportunity to deposit thin (less than 5 µm) and defect free gas-tight solid electrolyte layers based on stabilized zirconia. Physical and chemical deposition techniques (magnetron sputtering, PVD etc.)

are not productive enough and require expensive equipment. Aerosol deposition (4) is one the most promising techniques for this case.

Research group in Institute of Solid State Physics RAS conducts fundamental research and development activities in a field of solid oxide fuel cells (SOFC) and power plants based on them: new materials (5-6), membrane-electrode assemblies (7-9), protective coatings (10-11), glasses (12-13), electrode processes (14-18). In previous works we reported the results for manufacture technology development of SOFC membrane-electrode assemblies (MEA) with electrolyte support prepared via separate firing (7), co-firing at temperature close to optimal for cathode electrode (8), as well as close to optimal for anode electrode (9). MEA with anode support give opportunity to deposit thin-film electrolyte and to decrease the total resistance of SOFC with increase of power density. Substitution of electrolyte-supported SOFC with anode-supported structures in Institute of Solid State Physics RAS SOFC stacks gives opportunity to dramatically increase power output. In this work we describe results of optimization of solid electrolyte deposition routine via aerosol deposition developed in Institute of Problems of Chemical Physics RAS.

Experimental

Experimental techniques

Microstructure of materials (start and after different treatments) as well as ceramic samples was studied by means of scanning electron microscopy (SEM) using microscope Supra 50VP (Oxford Instruments) equipped by INCA Energy+ analysis system.

Grinding of solid electrolyte powders was carried out on a Fritsch Pulverisette 6 classic line planetary ball mill in a zirconium cup with zirconium balls (10 mm in diameter) for 2 hours. Rotation speed was controlled on a level of 400 rpm.

Anode supports for aerosol deposition

We used two types of anode supports in this work: pressed supports and commercially available Ningbo SOFCMAN Energy Technology Co., Ltd. (China) anode supports.

Pressed anode supports. Pressed supports were prepared using mixture of 60 wt.% nickel oxide (NiO) manufactured by Scientific and Production Company "T:SP", Ltd. (Russia) and 40 wt.% of 10Sc1CeSZ (89 mol% $ZrO_2 + 10 mol\% Sc_2O_3 + 1 mol\% CeO_2$) manufactured by Qingdao Terio Corporation (China). This mixture was ball milled using Fritsch 05.102 (Germany) in a mixture of toluene and butanol with the rotation speed of 100 revolutions per minute for 24 hours.

Ningbo SOFCMan Energy Technology Co., Ltd. anode supports. We used commercially available 2-layered NiO+YSZ supports with the thickness of about 400 um.

Solid electrolyte materials

In previous works we showed that zirconia electrolytes stabilized by about 10 mol% of scandia show maximal ionic conductivity in the SOFC operating temperature range (19-21). Despite of this we used 8YSZ powder as it is more easily available commercially.

We used YSZ (yttria-stabilized zirconia, $ZrO_2 + 8 \mod \% Y_2O_3$) powders manufactured by following companies:

- 1. GuangDong Orient Zirconic Ind Sci & Tech Co., Ltd. (China) sample 1, hereinafter GuangDong
- 2. Qingdao Terio Corporation (China) sample 2, hereinafter Terio
- 3. Ningbo SOFCMAN Energy Technology Co., Ltd. (China) sample 3, hereinafter SOFCMAN
- 4. "NeoChem", JSC (Russia) sample 4, hereinafter NeoChem
- 5. "CMP", JSC (Russia) sample 5, hereinafter CMP
- 6. Aldrich (USA) sample 6, hereinafter Aldrich

All the powders were analyzed using scanning electron microscopy (SEM) to study their microstructure. SEM images of three first powders (samples 1-3: GuangDong, Terio and SOFCMAN) from the list above with different magnifications (1kX and 100kX) are presented in figure 1 (GuangDong – top images, Terio – middle images and SOFCMAN – bottom images).



Figure 1. SEM pictures of YSZ powders: GuangDong (top images), Terio (middle images) and SOFCMAN (bottom images) obtained at different magnifications: 1kX and 100kX

One can observe from SEM images in figure 1, that all the powders presented (GuangDong, Terio and SOFCMAN) are formed by nanoparticles with the size of about 100 nm. These particles are formed in spherical granulates with size of about 30-50 μ m, these granules are quite easy to destroy by simple milling. Morphology of these powders is rather convenient for aerosol deposition.

SEM images of last powders (samples 4-6: NeoChem, CMP and Aldrich) from the list above obtained at different magnifications (1kX and 100kX) are presented in figure 2 (NeoChem – top images, CMP – middle images and Aldrich – bottom images).



Figure 2. SEM pictures of YSZ powders: Neochem (top images), CMP (middle images) and Aldrich (bottom images) obtained at different magnifications: 1kX and 100kX

One can observe from SEM images in figure 2 that NeoChem powder is formed by nanoparticles with the size of about 100 nm, particles are formed in agglomerates with the complex shape. CMP and Aldrich powders also consist of nano-scale particles with average size of about 100 nm. These particles are agglomerated. For CMP powders these agglomerates have large size – up to 10-20 um, and for Aldrich they have size of about 300-500 nm.

Aerosol deposition unit

In present work we used "cold" aerosol deposition in vacuum using supersonic jet of solid particles aerosol as the most promising technique for thin-film deposition of electrolyte layers for solid oxide fuel cells. This technique was developed in 90s years of the last century in Japan (22-23), it is based on the process of room temperature impact consolidation (RTIC).

Experimental setup developed and created in Institute of Problems of Chemical Physics RAS was equipped by highly-efficient vacuum pump system based on rotary pump with a mechanical booster AVD 150/25 with pumping speed of 150 l/s in the working pressure range of 50-600 Pa. Schematic diagram (left) and photo (right) of the setup is presented in figure 3.



Figure 3. Schematic diagam (left) and photo (right) of the setup used for aerosol deposition of thin-film solid electrolyte layers

Thin films were deposited in a vacuum chamber with the volume of 0.3 m^3 . Supersonic jet of solid particles aerosol was formed using Laval nozzle with axial symmetry with throat of 0.5 mm². The working vacuum during deposition was controlled at about 200 Pa. A thin-film coating was formed in the collision of accelerated particles with a support surface. The distance between the Laval nozzle and the substrate during the deposition of the electrolyte layer was 10 mm.

Nitrogen was used as a carrier gas. The gas-powder mixture was formed in an aerosol chamber with vortex flows of the carrier gas at an additional pressure of 0.05 MPa. The aerosol chamber was fixed on a vibrating platform with circular vibrations (shaker Vibramax 100, Heidolph, Germany). Circular vibration speed was controlled on a level of about 600 revolutions per minute, which was an optimal one to shake the powder and to form the aerosol.

The substrate was placed on the X-Y-platform with computer control (Jiangxi Liansheng Technology Co., China). To obtain an entire coating over a large area, the substrate was moved in the form of a rectangular raster with a step of 0.2 mm with subsequent passes with a rotation of the raster by 90°. The sweep speed of the substrate was 1 mm/s. The thickness of the deposited films was obtained after 4 deposition passes.

Results and discussion

Results of the first deposition tests

The application of granular powder for aerosol deposition in vacuum allows to fabricate exceptionally large ceramic thick films with areas of $1000 \times 800 \text{ mm}^2$ and with high deposition rates of more than 1 µm/min (24). In addition, Park et al (25) showed the possibility of deposition of dense optically transparent films from Al₂O₃ granules, the structure of which largely depends on the raw powder particle size. On the other hand, the presence of agglomerates in the aerosol jet leads to the formation of porous films with insufficient quality (4). Thus, all the powders described in section "Solid electrolyte materials" were employed to test for depositions using aerosol deposition setup. The GuangDong, Terio and SOFCMAN powders showed in figure 1 were successfully deposited, but the deposition rate showed a dependence on the origin of the powder. . GuangDong and Terio powders showed lower deposition rate. For this reason, only SOFCMAN powder was used further from the group of granulated compositions (from first three powders, showed in figure 1).

Aldrich and Neochem powders were also tested from the point of view of aerosol deposition, but we did not manage to reach the stable and quick deposition. CMP powder showed quick growth of thin film, and this powder was chosen as only one powder from the group of agglomerated compositions (from the last three powders showed in figure 2). So, as a result of test depositions, we have chosen SOFCMAN and CMP powder for further optimization of deposition process.

Deposition of initial powders without pre-treatment

Selected powders – SOFCMAN and CMP were deposited using aerosol deposition technique. Thin films deposited were sintered in air at 1350 °C for 4 hours. SEM-images of film surface (top images) and cross sections (bottom images) for SOFCMAN (left images) and CMP (right images) are shown in figure 4.



Figure 4. SEM-images of film surface (top images) and cross sections (bottom images) for SOFCMAN (left images) and CMP (right images)

One can observe from figure 4, that SOFCMAN powder gave opportunity to deposit a film with a thickness of about 50 μ m (figure 4 left bottom image). This film has large scale cracks with a size of about 30 μ m. We explain appearance of these cracks by shape and size of powder granulates (figure 1 bottom left image). We expect these granulates to collide the surface during deposition process and separate into smaller pieces to form the film. Large size of granulates did not give opportunity to form a dense film during deposition process. Cracks can be also observed from the surface view of film (figure 5 left top image).

CMP powder gave opportunity to form more uniform film, but this layer has much smaller thickness of about 5 μ m. One can also observe high porosity of this film caused by agglomerated powder morphology.

As all the difficulties of depositions were caused by powder morphology, we came to the conclusion about the necessity to mill the powders in ball-mill to destroy granulates (in case of the SOFCMAN powder) and dense agglomerates (in case of the CMP powder).

Deposition of pre-treatment powders

SOFCMAN and CMP powders were preliminary milled in planetary ball mill in zirconia cup with zirconia balls with the diameter of 10 mm for 2 hour. Rotation speed was controlled on a level of 400 rpm. Milled powders were deposited via aerosol deposition. SEM-images of film surface (top images) and cross sections (middle and bottom images) for different magnifications (2.5kX from middle and 5kX for bottom

images) for SOFCMAN (left images) and CMP (right images) powders after milling are shown in figure 5.



Figure 5. SEM-images of film surface (top images) and cross sections (middle and bottom images) for different magnifications (2.5kX from middle and 5kX for bottom images) for SOFCMan (left images) and CMP (right images) powders after milling

One can observe from figure 5 right images, that milling of CMP powder did not change the situation dramatically. Milling energy is not high enough to destroy the agglomerates. Film deposited is still porous.

Milling of SOFCMAN powder changed the film quality dramatically. As a result, we managed to deposit a thin film with small defects, their size is much lower than film thickness. So, one needs to avoid the existence of dense agglomerates to form the dense film via aerosol deposition.

Cathode deposition and electrochemical performance of model SOFC will be described in future manuscripts elsewhere.

Conclusions

In this work we describe an experience of thin film deposition of dense gas-tight solid electrolyte membranes for SOFCs via aerosol deposition in vacuum. We tested different YSZ solid electrolyte powders manufactured by GuangDong Orient Zirconic, Qingdao Terio Corporation, Ningbo SOFCMAN Energy Technology (three granulated powders); NeoChem, CMP and Aldrich (three agglomerated powders). SOFCMAN and CMP were chosen as most promising powders from each morphology group. It was shown that the use of granular powders (such as SOFCMAN) allows to obtain coatings with a high deposition rate (thickness of 50 µm for 4 passes at the sweep speed of 1 mm/s). On the other hand, the deposition of the granular powders leads to the formation of films, which even after annealing have a defective structure containing large pores and channels. Planetary ball milling dramatically changes the situation for granulated SOFCMAN powder, as this routine gives opportunity to destroy granules and form a dense gas-tight uniform film. As for CMP, ball milling does not lead to so dramatic changes as ball mill energy is not sufficient enough to destroy the agglomerates. So, one needs to avoid the existence of dense agglomerates to form the uniform gas-tight film via aerosol deposition. Electrochemical performance of model SOFC with solid electrolyte membrane deposited via aerosol deposition will be described in future manuscripts elsewhere.

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