CIP-BASED FABRICATION OF SOFC CERAMIC COMPONENTS FROM OXIDE NANOCRYSTALLINE POWDER MATERIALS

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Abstract: Cold isostatic pressing approach has been applied to fabricate three-layered ceramic sandwich membranes for SOFC from nanocrystalline oxide powders. Advantages and problems inherent to the method are revealed and discussed, the ways of the problem solutions are envisaged. Prototypes of the membranes are manufactured.

Key words: Solid Oxide Fuel Cells/Zirconia/Cold Isostatic Pressing.

1. INTRODUCTION

Energy consumption and, in particular, electric power consumption continues to grow around the world. Because of it, novel more efficient technologies of energy production are needed. Fuel cells, chemical energy sources able to convert directly the energy of fuels into the electric power, are among the most promising ones in this respect. Although fuel cells were discovered about 150 years ago, a related market has been formed only during last two decades on the base of intensive research and development activities in all technological fields including simulation, design, and development of new materials.

N. Sammes et al. (eds.), Full Cell Technologies: State and Perspectives, 175-180.

Solid oxide fuel cells (SOFC) constitute one class of the chemical sources. SOFC ensure much more effective electric power production and environmental safety as compared with conventional power generation technologies [1,2,3].

The main component of a solid oxide fuel cell is a three-layered sandwich consisting of anode, electrolyte, and cathode, each being made from a different oxide ceramic material. Such ceramic structures can be fabricated by various methods including slip or tape casting, injection molding, ceramic coverings, etc. [1]. Whatever the method applied is, it should provide the best able microstructure and specified performance of materials besides the desired shape of a SOFC membrane. However, layers of the membrane have different properties that requires combination of two or more different methods of ceramic engineering in the component fabrication.

Cold isostatic pressing (CIP) can be one of such methods [1]. In the case of SOFC components, it has advantages of:

- easy microstructure management using CIP pressure optimization;
- porosity control in anode and cathode materials;
- perfect contact between layers of the sandwich;
- no need in organic binders (with an exception of pore-forming agents) in initial powders and, as a result, a shorter sintering time;
- high production rate of the process;
- fabrication of both flat and cylindrical shapes for planar and tubular fuel cells, respectively.

Moreover, it is known that the CIP procedure involves lowering of the sintering temperature by 100 to 200°C for many ceramic materials including those applied in fuel cells [1].

The goal of the present work was CIP application for manufacturing three-layered ceramic structures from nanocrystalline powders and determination of characteristics of the involved ceramic materials immediately affecting on performance of resulting membranes.

2. MATERIALS AND PROCEDURES

The expected layout of the work consisted in the fabrication of three-layered ceramic membranes with 30 to 35 mm in diameter, see Fig.1.

All three layers, namely porous anode, electrolyte, and cathode, were manufactured from agglomerated ceramic powder ZrO_2 + 8 mol.% Y_2O_3 with a crystallite size from 10 to 20 nm. The anode and cathode materials were doped with 50 wt.% nickel oxide and 50 wt.% lanthanum manganate, respectively. Taking into account that the sintered electrolyte material should be gas-tight

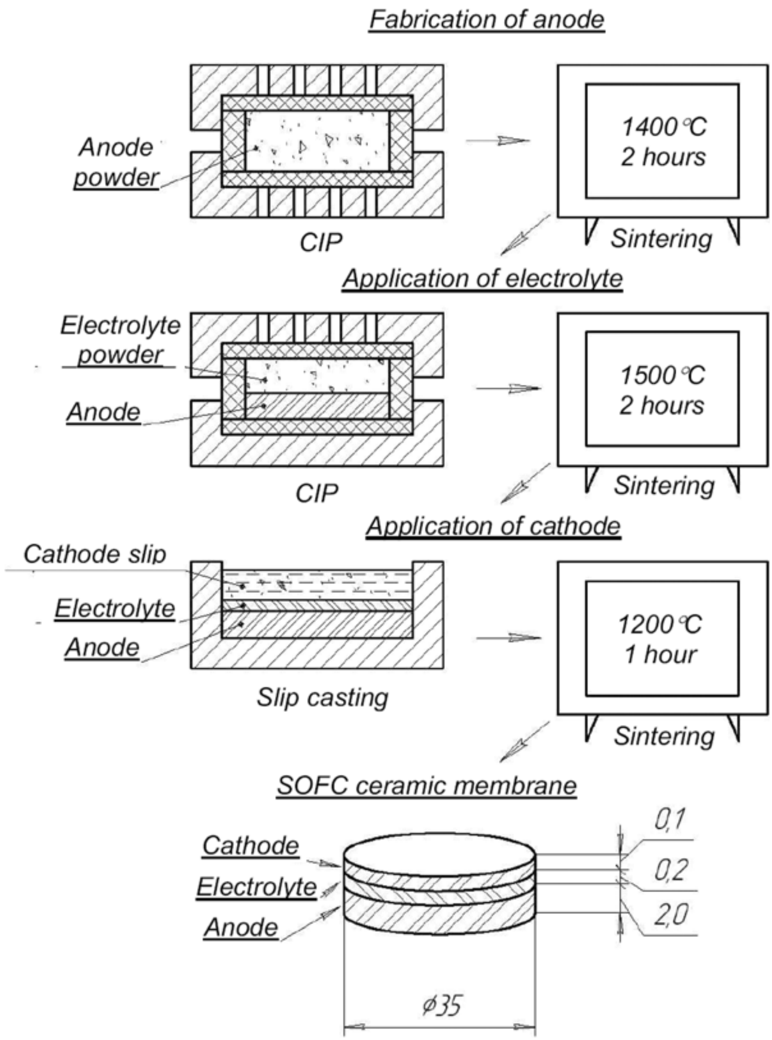

Figure 1. Flow chart of SOFC three-layered membrane manufacturing process based on CIP.

while anode and cathode materials have to be gas permeable, a powder material of anode was mixed with 10 or 30 wt.% of starch as a pore-forming agent, whereas the cathode layer was made porous using low sintering temperature.

Selection of the most perfect and reliable electrolyte-anode adjoining method based on CIP techniques was performed as follows. Anode and electrolyte layers in various conditions (press-powder, green compact, partially sintered compact, or sintered ceramics) were jointly isostatically pressed at pressure values from 0.05 to 0.8 GPa. Since the electrolyte layer should be much thinner than the anode one, such joint isostatical pressing, as a rule, had a nature of adpressing the electrolyte powder onto a pre-formed anode compact. The two-layered plate produced by such a way was sintered at 1500°C. Thereafter a cathode layer was build up in a similar manner. Alternatively the cathode layer was applied by molding a slip prepared from a mixture of the powder and alcohol. A green cathode layer on the plate was sintered at 1200°C.

3. RESULTS

It was found that the layer adjoining performance was always unsatisfactory at adpressing either electrolyte onto sintered anode or cathode onto sintered electrolyte. It was caused probably by high hardness of the sintered ceramics preventing good adhesion of adpressed powder particles.

Satisfactory results were obtained by adpressing an electrolyte layer onto a pre-compacted anode layer or at slip painting the powder cathode onto a partially sintered electrolyte. A flowchart of the developed process for manufacturing ceramic membranes using the CIP procedure is presented in Fig. 1.

Experimental studies have shown that a number of problems can occur due to different shrinkage values in anode and electrolyte compacts during joint CIP or sintering, including bending, buckling, delamination, splitting along anode and electrolyte layers interface, and/or radial cracking of plates.

Bending or buckling are caused generally by mismatching shrinkages of the adpressed materials. It was found experimentally that these phenomena can be fully or partially eliminated by means of:

- strengthening the green anode with preliminary partial sintering at temperatures below 1500°C;
- thinning the adpressed layer of electrolyte;
- matching shrinkages of both jointly pressed powder materials;
- implementing the composite rubber/metal pressforms strictly confining the compacts and precluding any bending or buckling.

On the contrary, splitting or delamination are obviously connected with weak cohesion between anode and electrolyte layers. Numerous experiments have shown that such delamination at pressing can be precluded in the following ways:

- increasing a porosity of anode (in the present work the content of the pore-forming agent was increased from 10 to 30 wt.%);
- weakening granules of the adpressing electrolyte powder or, in other words, reducing coherence of individual particles, by means of modifying processes of re-granulation and drying of initial powder materials.

In its turn, delamination at sintering originates from the low strength of the anode material. It follows from splitting the anode layer instead of separating anode and electrolyte as a cause of delamination.

Experimental process optimization by selecting the best CIP pressure, anode sintering temperature, and pore-forming agent content has enabled to fabricate prototypes of two-layered (anode/electrolyte) and three-layered (anode/electrolyte/cathode) membranes, see Fig. 2.

Figure 2. Three-layered SOFC membrane.

Final examinations and measurements have shown that anode and cathode have open porosity at the level of about 35% while the electrolyte is virtually poreless. Scanning electron microscopy of the sandwich fracture surface has revealed only small closed pores below 0.01 μm in the electrolyte layer.

4. CONCLUSIONS

The present work has confirmed good perspectives for the CIP application to fabricate multi-layered membranes for fuel cells by building-up the electrolyte layer onto green anode.

Successful application of the developed process for membranes production requires:

1. Matching shrinkages of the powder materials in use.
2. Providing free-flowing powders suitable to form very thin layers.
3. Providing powders with 'soft' granules.
4. Designing rigid pressforms preventing bending or buckling of compacts at pressing.
5. Providing sintering of virtually poreless electrolyte ceramics at relatively low (about 0.15 GPa) CIP pressures.

Implementation of the CIP route at the SOFC membrane production ensures a good cohesion between anode and electrolyte layers and high strength and thermal shock resistance of the electrolyte.

Further work in this direction is connected with lowering the sintering temperature of electrolyte ceramics accompanied by simultaneous increase of the isothermal exposure time. Lower sintering temperature can result in smaller grain sizes at the same high density of ceramics that could improve such characteristics of membranes as current density and thermal stability.

ACKNOWLEDGMENT

Many thanks to Prof. *V.G.Vereschak* and Dr. *A.Yu Koval* for their invaluable contributions.

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