THIN ELECTROLYTE LAYERS FOR SOFC
VIA MODIFICATION OF CERAMIC MEMBRANES
BY CVD AND EVD

Y.S. Lin, L.G.J. de Haart, K.J. de Vries
and A.J. Burggraaf
Laboratory of Inorganic Chemistry, Materials Science
and Catalysis, University of Twente, P.O.Box 217
7500 AE Enschede, The Netherlands

ABSTRACT

The efficiency of state-of-the-art solid oxide fuel cells can be improved by applying YSZ electrolyte layers with thicknesses reduced to a few micrometers. This will allow the operating temperature of reactors made of these SOFC's to be lowered to 800 - 900 °C. The membrane-based thin electrolyte layer SOFC technology is therefore being developed. A ceramic membrane is deposited on and integrated with the supported porous cathode layer. A modified-CVD process combined with an Electrochemical Vapor Deposition (EVD) process is used to grow a (very) thin gas tight YSZ layer on this composite layer system. Preliminary experimental depositions on alumina substrates show the formation of a gas tight YSZ layer (thickness of a few microns) after 6 hours of deposition.

1 INTRODUCTION

Solid oxide fuel cells (SOFC) reactors are attractive energy conversion systems. They have a very reasonable efficiency compared to the conventional systems based on fuel combustion. Increase in usefulness of SOFC reactors can be achieved when the limitations of presently developed reactors can be avoided or at least decreased. There are two main limitations. The first is related to the use of cubic yttria-stabilized zirconia (YSZ) as electrolyte. The value of the (specific) conductivity of this material requires SOFC reactor operating temperature of 1000 °C in order to reach an acceptable high conductivity of the applied electrolyte layers, which have a thickness of about 60 - 150 μm. This high operating temperature lowers the obtainable OCV considerably. The second limitation is the perovskite-type cathode material, usually Sr-doped LaMnO₃, which causes too high electrode polarization losses, besides ohmic I*R losses, when the current path from the electrolyte/electrode interface through the cathode layer to the interconnection material (ICM) is too long.

In this contribution we present the membrane-based thin YSZ electrolyte layer SOFC technology. We aim to present a technology to reduce the layer thickness of the presently applied YSZ electrolyte layers to thicknesses of a few microns or less. This will decrease the ohmic polarization losses. Such a considerable reduction of the electrolyte layer thickness will allow the SOFC reactors to be operated at lower temperatures (800-900 °C).

These (very) thin electrolyte layers require to be supported when produced. A suitable production technique for thin supported YSZ layers is Electrochemical Vapor Deposi-
tion (EVD). The EVD technique has been used (1-3) demonstrating its unique ability to form relatively thin gas tight YSZ films on porous substrates. In order to apply EVD in the production of very thin gas tight YSZ layers, a ceramic toplayer with porous membrane characteristics has to be developed.

The procedure for constructing the membrane-based thin electrolyte layer SOFC includes: (i) deposition of a (thin) porous cathode layer on a coarse-pore ceramic support; (ii) deposition on and integration with the supported porous cathode layer of a porous ceramic toplayer with membrane properties; (iii) growth of a very thin and gas tight YSZ layer by a combined CVD and EVD procedure onto the supported porous membrane toplayer and (iv) providing a porous anode layer by filmcoating onto the thin gas tight YSZ layer.

The deposition process of YSZ starts with a CVD step in which YSZ is deposited in the membrane pores due to the reaction between water vapor and a mixture of ZrCl₄ and YCl₃ vapor in a desired ratio. The two separate gas streams, one with the chloride vapors and one with the water, enter the system from the membrane side and from the coarse-pore support side respectively. After closure of the membrane pores by the formation of a YSZ plug, layer growth starts due to the EVD process (3,4).

In the present investigation we report on the theoretical study of the kinetics of the EVD phase of the deposition process and on preliminary experimental results of growing thin YSZ films on porous alumina substrates.

2 THEORETICAL AND EXPERIMENTAL

An important aspect of the CVD phase of the YSZ deposition in the membrane pores is, that plug formation in the pore occurs near the upper surface of the membrane toplayer, i.e. near the surface of the supported system at which the metalchloride mixture is delivered. Then the formed gas tight YSZ layer can be kept as thin as possible.

Mathematical analysis (4) shows that the CVD process is mainly determined by six independent parameters. The main parameter governing the location of pore-closure in the membrane toplayer is the Thiele modulus $\phi$. Approximately the Thiele modulus can be considered to be proportional to the ratio of the reaction rate constant ($K$) to the effective pore diffusivity for the metalchloride mixture ($D_{cg}$):

$$\phi = \frac{K}{D_{cg}}$$  \hspace{1cm} (1)

A larger Thiele modulus results in location of pore-closure nearer to the metalchloride delivery side.

In the EVD phase of the YSZ layer deposition process the film growth is determined by four mass transfer steps: (i) water (or oxygen) diffusion in the substrate pore, (ii) charge-transfer reaction at the interface between the EVD film and the water vapor, (iii) electrochemical transport in the EVD layer and (iv) charge-transfer reaction (formation of solid oxide) at the interface between the EVD film and metal chloride vapor. Assuming a quasi steady-state and using Wagner-type approach, the kinetics of the EVD film growth is described by a mathematical model which considers all four mass transfers.

From the solution of the model it is found, that the function of EVD film thickness versus deposition time, $H(t)$, is parabolic only when electrochemical transport in the growing
EVD film is the rate-limiting step:

$$H(t) = k_0/t$$  \hspace{1cm} (2)

If any one of the other three mass transfer steps is the rate-limiting step, \(H(t)\) should be a linear relation. Mathematical analysis further shows that the rate-limiting step for deposition of YSZ on the porous substrate under the conditions as reported previously (1,3) as well as in the present investigation is water (oxygen) diffusion in the substrate pore.

As a preliminary experimental investigation, the EVD experiments were concentrated on the deposition of YSZ layers on porous alumina substrate disks. The experiments were performed in a CVD/EVD apparatus. The main part of the apparatus is an alumina tube reactor heated by a six zone furnace. All the experimental conditions such as reaction zone temperature, gas delivery and system pressure could be controlled in this apparatus. Typical experimental conditions were: total concentration of metal chloride vapor = \(2.0 \times 10^{-9}\) mol/ml; \(\text{YC}_3/\text{ZrCl}_4\) ratio in vapor phase = 1:5; total pressure in reaction zone = 1.5 mbar; total water vapor concentration = \(3.5 \times 10^{-9}\) mol/ml and the deposition temperature = 1000 °C. The two substrates used were porous alumina disks with mean pore sizes of 11.0 and 0.16 \(\mu\)m, respectively. The deposition results were characterized by XRD, SEM and EDS.

It was found, that after 6 hours deposition (or longer) a gas tight YSZ layer was formed on the side of the substrate exposed to the metal chloride vapor. The XRD and EDS data show that this layer has a FCC crystal structure with an \(\text{Y}_2\text{O}_3/\text{ZrO}_2\) ratio of about 8%. This is apparently being determined by the \(\text{YC}_3/\text{ZrCl}_4\) ratio in the metal chloride vapor. The deposit of the solid oxide penetrates only a few microns deep into the substrate pores. Figure 1 shows a SEM photograph of a deposit. The deposited film thickness is in the range of a few microns. The deposition time required for depositing approximately the same thickness of EVD film on two substrates with different pore-sizes was determined in order to examine the predictability of the film growth theory. Based on these preliminary experimental results, as well as on theoretical understanding of the film growth kinetics, the deposition of the solid electrolyte layer by the EVD process will be optimized.

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REFERENCES

(1) A.O. Isenber, ECS Symp. Electrode Materials, Processes for Energy Conversion and Storage, Vol. 77-6 (1977) 572
(2) G. Dietrich and W. Schäfer, J. Hydrogen Energy 9 (1984) 747
(3) M.P. Carolan and J.N. Micheals, Solid State Ionics 25 (1987) 207
(4) Y.S. Lin, K.J. de Vries and A.J. Burggraaf, accepted for presentation at EURO CVD 7, June 19-23, 1989, Perpignan, France
(5) P. Kofstad, High Temperature Oxidation of Metals, Ch. 5, Wiley (1966)
FIGURE 1

SEM photograph of a CVD/EVD deposit of yttria-stabilized zirconia (YSZ) on a porous alumina substrate. The left-hand side of the picture shows the YSZ deposit, while the fracture surface of the alumina substrate is visible on the right-hand side. Near the fracture surface the YSZ deposit has been peeled off, leaving still a small part of the deposit visible at the top-center of the picture.