SOFC BASED ON THIN-FILM ELECTROLYTE

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ABSTRACT

Solid oxide fuel cells (SOFCs) with thin-film electrolyte were fabricated and tested. MOCVD technique was applied for deposition of thin YSZ electrolyte films with thickness of 4-15 μm on porous Ni-YSZ anode substrate. Volatile complexes of metals with 2,2,6,6-tetramethylheptanedione: Zr(thd)4 and Y(thd)3 were used as the precursors. Cells exhibited a high open circuit voltage of 1.08 V and power density higher than 200 mW/cm² at 800°C.

INTRODUCTION

Conventional YSZ-electrolyte-supported SOFCs are operated at temperatures about 1000°C in order to attain reasonable power. Such high temperatures cause a number of problems including interdiffusion between electrodes and electrolyte, as well as mechanical stress due to different thermal expansion coefficients. All these problems have limited commercial development of SOFCs. Use of thin-film electrolytes with thickness of about 10 μm allows decreasing the cell operating temperatures to 800°C. Lower temperature operation allows a broader choice of interconnect materials, including metal alloys, as well as decreasing mechanical stress and rate of solid phase reactions. This will allow production of intermediate-temperature SOFCs with lower cost and higher lifetime.

At present many deposition techniques are used for production of thin-film electrolytes (1). CVD (Chemical Vapor Deposition) is one of the most challenging and practically feasible methods (2). Using this method, high-quality electrode-supported thin-film electrolytes with thickness of 40 μm were obtained by Siemens Westinghouse using chlorides of Y and Zr as precursors (3). However, application of these compounds in CVD processes has a number of disadvantages, such as high temperature of deposition process and presence of corrosive gases, which requires expensive equipment and prevents commercialization of SOFCs.

MOCVD (CVD using volatile Metal compounds with Organic ligands as the precursor) is the alternative CVD technique because of its lower operation temperature and suitability to prepare thin film electrolytes. Precursors in the MOCVD technique contain no chlorine. Metal alkoxides and β-diketones have been used as the precursors for preparing YSZ films by means of MOCVD (1, 4-6).
In this work we present our experiments on fabrication of SOFC based on YSZ thin-film (4-15 μm) electrolytes obtained by the MOCVD technique. Volatile complexes of metals with 2,2,6,6-tetramethyl heptanediione: Zr(thd)₄ and Y(thd)₃ were used as the precursors for film deposition processes. Electrolyte films were deposited on porous anode substrates. Cells with thin-film electrolyte were fabricated and tested.

**EXPERIMENTAL**

Fig. 1 shows a schematic view of the deposition process by means of the MOCVD technique. Zr(thd)₄ and Y(thd)₃ precursors are loaded into vaporization chambers. During heating, the compounds are transferred into gaseous phase and transported by carrier gas (Ar) through warmed-up pipeline towards the substrate surface. Reagent gas (oxygen) is supplied directly to the deposition zone. It is possible to conduct deposition of YSZ films with controlled Zr/Y proportion (in the electrolyte film) using two separate vaporization chambers with independent heaters for Zr(thd)₄ and Y(thd)₃.

Temperature of the Y(thd)₃ vaporizer varied in the range of 120-140°C, and vaporization process of Zr(thd)₄ was conducted at 150-215°C. Argon flow was 1-3 l/h, oxygen flow was 2-15 l/h. Total pressure in the reactor was 10 Torr. YSZ electrolyte films with thickness of 4-15 μm were deposited on porous anode substrates (YSZ/NiO) at temperatures of 600-700°C. Deposition rate was 0.5-3.5 μm/h. Green anode substrate was prepared from the powder mixture of 8 mol% YSZ (50%) and NiO (50%). The powder mixture was compacted under uniaxial pressure into disks with diameter of 18 mm and thickness of 1 mm and baked at 1350°C for 1 hour.

Scanning electron microscopy SEM (LEO 430 VP) was employed to observe the thin-film cross-section. Element composition of the films was analyzed by the X-Ray-fluorescence microprobe method (OXFORD 7353).

SOFCs were fabricated and tested with thin films obtained by MOCVD, Fig. 2. Catalyst layer of La₀.₈₅Sr₀.₁₅MnO₃ with thickness of about 100 μm was applied onto the electrolyte film and sintered in the air at T=1200°C for about 1.5 hour. Current collector (platinum mesh) was baked at 1000°C to the cathode using platinum paste. Platinum wires were attached to the platinum mesh. Fabricated SOFC was assembled and sealed to alumina tube using a glass seal with softening temperature of 960°C and operational temperature of 750-940°C.

Cell was heated up to 960°C, as assembling and sealing took place in the air. Afterwards, temperature was decreased down to 780°C, as the tube volume was vented with argon. Wet hydrogen (4% H₂O) was used as fuel. During the experiment hydrogen flow was 0.5 cm³/s.

**RESULTS**

Parameters of the MOCVD method (temperatures of vaporizer and substrate, gas pressure in the reactor, etc) allow conducting the process at various deposition rates and to obtain thin films with different compositions. These factors determine in turn the structure of
YSZ films obtained. By varying the vaporization and mass transfer conditions of precursors, composition optimization of thin film electrolytes was conducted. Thin films with homogeneous distribution of Zr and Y oxides along all thickness were obtained. Data on film composition by means of X-Ray fluorescence technique are shown in Fig. 3. One can see that the Zr/Y proportion in film virtually coincides with the anode components proportion.

Varying mass transfer rates of the precursors and deposition temperature, YSZ thin-films with different structures were obtained on porous anode substrates. Films obtained at relatively high deposition rates (about 3 μm/h) had columnar structures (Fig. 4(a)). Films obtained at lower deposition rates (0.6-1 μm/h) had compact structures (Fig. 4(b)).

SOFCs were produced with compact structure YSZ films obtained at optimum deposition conditions. Fabricated SOFCs have Ni – YSZ / YSZ / Lao.8Sro.15MnO3 structure. After anode reduction within 4 hours, open circuit voltage (OCV) was 0.98-1.08 V. Such high OCV value indicates that the deposited YSZ electrolyte films have low leakage.

One can see that power density reaches 200 mW/cm² at 780°C and more than 600 mW/cm² at 937°C. The thin-film fuel cells have been tested for 1000 hour and have been thermally cycled from 780 – 940°C while showing no performance deterioration.

**CONCLUSIONS**

High-quality anode-supported YSZ electrolytes with thickness of 4-15 μm were obtained by the MOCVD method using chlorine-free precursors. MOCVD method allows producing low-leakage anode-supported thin-film YSZ electrolytes at temperatures about 700°C. Substantial advantage of this method is the fact that the film synthesis temperature nearly corresponds to the SOFC operational temperature, which essentially decreases mechanical stress in the film-electrode system and leads to extension of the SOFC lifetime. This method is very effective technologically and can be applied for manufacturing of SOFCs with thin-film electrolytes.

Our future work will be focused on production of large-area (100 cm²) YSZ and CGO electrolyte SOFC. On the basis of such SOFCs, a 1 kW stack is planned.

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![Figure 1. Schematic representation of CVD process.](image1)

![Figure 2. Schematic of fuel cell test apparatus.](image2)

![Figure 3. Microprobe XRF analysis of Zr/Y distribution in the thin-film electrolyte.](image3)

**Figure 1.** Schematic representation of CVD process.

**Figure 2.** Schematic of fuel cell test apparatus.

**Figure 3.** Microprobe XRF analysis of Zr/Y distribution in the thin-film electrolyte.
Figure 4. SEM cross-sectional images of NiO-YSZ anode and YSZ films of electrolyte deposited by MO CVD process.

Figure 5. I-V and power curves of the fuel cell with thin-film electrolyte.