CO-SINTERING OF DENSE YSZ ELECTROLYTE FILMS ON POROUS NiO-YSZ SUPPORTING ANODES FOR IT-SOFCs

Giuseppe Savo, Alberto Rainer, Alessandra D’Epifanio, Silvia Licoccia and Enrico Traversa
Department of Chemical Science and Technology
University of Rome Tor Vergata, 00133 Rome, Italy

ABSTRACT

A process for the preparation of anode-electrolyte assemblies for IT-SOFCs is presented. This process involves the preparation of a green membrane of NiO-YSZ and subsequent electrophoretic deposition (EPD) of commercial YSZ powder on this polymer-rich membrane. A single thermal treatment allowed removal of the organic compounds, sintering of the layers and full densification of the electrolyte.

INTRODUCTION

One of the main research objectives in the field of solid oxide fuel cells (SOFCs) is the attempt to reduce the operating temperature from 1000°C down to 750°C or lower. The reasons for temperature reduction are mainly due to cost decrease and improvement of long term stability. To ensure a good power density, the ohmic resistance of the electrolyte must be lower than 0.15 Ω cm². In the case of YSZ, this resistance value can be reached at 700°C with a thickness of 15 μm. YSZ layers with such a thickness can be obtained by depositing high-quality dense films on porous supporting electrodes (1).

Several approaches have been reported in the literature for the deposition of YSZ films: electrochemical vapour deposition (EVD) (2), low pressure plasma spraying (3,4), RF sputtering (5), and colloidal processes such as slurry-based dip or spray coating (6). In this work, electrophoretic deposition (EPD) was selected as a technique to obtain thin dense electrolyte films. EPD is a well known process that allows obtaining compact ceramic coatings with thicknesses ranging from few micrometers to several millimeters (7,8), which has been used also for the preparation of YSZ electrolyte films in SOFCs (9-14).

This paper reports a different approach from the early papers that combines EPD with a co-sintering process. Co-sintering has recently been investigated as a promising technique for the reduction of the number of thermal cycles needed for the preparation of SOFCs (15, 16). However, substrates are usually pre-fired at an intermediate temperature prior to deposition and co-sintering. In this work, a one-step process for the sintering of a bi-layer assembly obtained by EPD of YSZ film directly on green NiO-YSZ membranes is presented.
EXPERIMENTAL

75 wt% of a commercial anodic powder, based on a mixture of NiO and YSZ (Praxair, 8 mol% YSZ, 5.3 m²g⁻¹, d₉₅ = 5.4 µm) was mixed with 20 wt% polyvinylidene fluoride (Solvay PVDF SOLEF 6020-1001), and 5 wt% of nano-sized carbon powder (Carbon Belgium, SuperP), and then dispersed in N-methyl-2-pyrrolidinone (Aldrich, 99% pure). The slurry obtained was spread on a glass pane yielding a green membrane with a thickness of approximately 750 µm. Circular bodies of about 15 mm diameter were cut from the membrane and used as substrates for EPD experiments.

A suspension of commercial YSZ powder (Tosoh, TZ8Y, 8 mol% YSZ, d₅₀ = 2 µm) in methanol was prepared by sonication. The cell used for the EPD experiments had a vertical setup. The substrate was connected to the negative electrode since YSZ particles in methanol are positively charged (8). The distance between the current collectors was 10 mm, while the volume of the plating bath was 60 mL. A constant 100 V DC voltage was applied for a deposition time of 8 minutes, monitoring the current during the experiment. After the deposition, the samples were dried at room temperature before the co-sintering process.

Thermogravimetric and differential thermal analyses (TG-DTA, Netsch STA 419) were performed on the green anodic membrane to evaluate the burn-out of the organic compounds. Co-sintering of the anode-electrolyte bi-layer was performed in air at a temperature of 1350°C, with a stop at 650°C to complete the burn-out of volatile compounds.

An anodic green substrate with no deposited film was added to each sintering batch, to serve as a reference for porosity investigation. Mercury porosimetry (Carlo Erba Instruments, Micropores 2000) was performed on uncoated sintered anodes to characterize the pore size distribution.

Field emission scanning electron microscope (FE-SEM, Leo Supra 1535) analysis was used to investigate the morphology of the layers. Energy Dispersion Spectroscopy (EDS, Oxford Instruments) was used to obtain compositional maps of the sintered bodies.

RESULTS AND DISCUSSION

The paramount step in the co-sintering process is the strict control of thermal treatments that cause oxidative decomposition of volatile compounds in the green substrate. A vigorous gas release during heating can determine the spalling of the coating and the formation of huge cracks. TG-DTA was used with the purpose of determining the proper thermal treatment to guarantee a uniform and slow burning process. Figure 1 shows the TG-DTA curves on a sample taken from a green membrane. An initial weight loss of about 15 wt% can be observed, which ends slightly above 100°C. This loss can be attributed to physisorbed water. The weight loss started again at 300°C and ended at 600°C, in three different steps accompanied by three exothermic peaks. This loss can be attributed to the thermal decomposition of the organic binder. Therefore, during the sintering, a very slow heating rate was maintained up to 650°C to ensure a slow burning process.
During sintering, evaporation of nickel oxide can occur, resulting in a compositional change of the sintered bodies. Figure 3 shows the results of EDS analysis performed on the starting powder (Fig. 2a) and on a large area of the anode (about 80 x 60 μm) after sintering (Fig. 2b). As can be observed, the ratio between YSZ and nickel is only slightly affected by the thermal treatment. This means that a very small nickel loss takes place, which does not compromise the catalytic activity of the anode materials in operating conditions.

Figure 2. EDS analysis of the commercial NiO-YSZ powder (a) and of the anode substrate fired at 1350°C for 6 hours (b).

Figure 3 shows the results of mercury porosimetry on an anode support sample sintered at 1350°C for 6 hours. The sample shows a large total porosity value after the sintering process, with a distribution of pore size spread in 1-10 μm range. The selected thermal treatment is therefore able to maintain the required porosity.
Figure 3. Pore size distribution for the anodes sintered at 1350°C for 6 hours.

For the deposition of the dense YSZ film by EPD on the green anodes, a number of experiments were performed to optimise the parameters controlling the electrophoretic deposition process of YSZ powder (17). Several variables were considered, such as applied potential, deposition time, particle loading and selection of solvent. The right choice of the solvent proved to be one of the key parameters. As reported in the literature (13), ethanol is often used since it has a quite slow evaporation rate, so the risk of fractures when the green deposit dries is low. However, better results were obtained using methanol instead of ethanol, probably because methanol is slightly more acidic than ethanol and has a lower viscosity. Best results were obtained using a suspension of 1 wt% YSZ in methanol, and performing EPD with a constant 100 V DC voltage applied for a deposition time of 8 minutes. After the deposition, the samples were dried at room temperature before the co-sintering process.

Figure 4 shows the top and the cross section view of the YSZ film deposited by EPD on a green NiO-YSZ substrate after co-firing at 1350°C for 6 hours. This is the same thermal treatment used previously to produce the porous anode substrate. After the co-firing process, a fully dense YSZ film with a thickness of 6-8 μm was produced, while the substrate kept its porosity. The adhesion between film and substrate was excellent, as shown in Figure 4b. Only a few submicrometric close pores can be observed in the cross section of the electrolyte, but their presence did not compromise its gas tightness. The small changes in thickness observed along the sintered YSZ film was probably due to the growth mechanism of the YSZ layer on the substrates during EPD; in fact, as seen with other colloids (18, 19), the growth can occur by aggregation of particles in “islands” under the influence of lateral forces, progressively covering the substrate.

Figure 5 shows the EDS Ni mapping together with the line scan for Ni Kα radiation for the same cross section as in Fig. 4b. No significant contamination of the electrolyte due to the evaporation of nickel oxide during sintering was observed.

The obtained thickness for the YSZ layer, below 10 μm, is compatible with a possible operation of the SOFC at 700°C or below, which was the target of this work.
CONCLUSIONS

An original process is presented to produce SOFCs with electrolyte thickness lower than 10 μm on supporting NiO-YSZ anodes starting from commercial powders, compatible for SOFC operation at intermediate temperatures. The combination of electrophoretic deposition and co-sintering is successful to produce anode-electrolyte assemblies with a single thermal cycle, depositing the electrolyte film on a polymer-rich anodic membrane. After co-sintering, the anode shows large porosity and the electrolyte is fully dense. Morphological evaluation of the deposited YSZ films demonstrated the absence of cracks and a very good adhesion of the film to the anode substrate. The diffusion of nickel through the electrolyte thickness was negligible. The possibility to use a single sintering step for the half cell and commercially available powders makes this method very promising for reducing manufacturing time and cost of SOFC components.
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