SOLID OXIDE FUEL CELLS WITH YSZ FILMS PREPARED USING SPRAY PYROLYSIS

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ABSTRACT
Spray pyrolysis technique has been applied to deposit thin, dense electrolyte films on porous anode substrates. Thin film deposition using spray pyrolysis involves the spraying of a metal salt solution onto a heated substrate. Two different atomizers were used for generation of aerosol; an electrostatic atomizer and an air blast atomizer. Solutions of yttrium chloride and zirconium acetylacetonate in butyl carbitol and ethanol mixtures were used as precursors. The 8 mol% yttria stabilized zirconia (YSZ) films were deposited on porous NiO-YSZ anode substrates which were heated to temperatures between 280°C and 320°C. Dense, submicrometer and crack-free electrolytes on substrates with diameters of up to 35 mm were prepared. Fuel cell tests were performed using dry hydrogen as fuel and air as oxidant. A power output of ~550 mW/cm² at 770°C was achieved.

INTRODUCTION
Spray pyrolysis is a processing technique to prepare thin and thick films, ceramic coatings, and powders. Unlike many other film deposition techniques, spray pyrolysis represents a simple and cost-effective processing method. It does not require high quality substrates or chemicals. Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, and temperature controller. The following atomizers are usually used in spray pyrolysis technique: air blast (liquid is exposed to a stream of air) (1), ultrasonic (ultrasonic frequencies produce the short wavelengths necessary for fine atomization) (2), and electrostatic (liquid is exposed to a high electric field) (3).

Thin YSZ films have already been deposited by spray pyrolysis on the following substrates: glass (4, 5), aluminium (6), steel (7), and porous La(Sr)MnO₃ cathode (8, 9). Setoguchi et al. deposited calcia-stabilized zirconia (15 at% CSZ) onto porous La₀.₈Sr₀.₂MnO₃ cathode substrates (10). The electrolyte was also deposited by YSZ powder suspension spraying with a high deposition rate (11). Choy et al. were able to deposit the complete cells using spray pyrolysis; however no data on electrochemical performance of the cells were presented (12). To our knowledge, only few reports on fuel cell tests have been published. A SOFC cell with a Ni-YSZ anode/15 at% CSZ electrolyte / La₀.₈Sr₀.₂MnO₃ cathode arrangement has been tested by Setoguchi et al. (10).
The tests were performed using hydrogen as fuel and oxygen as oxidant. The open circuit voltage (OCV) of the cell with 33 μm thick CSZ film deposited at 100°C was 960 mV and the maximum power density was 500 mW/cm² at 1000°C. Also 18 μm thick YSZ films have been tested using the same arrangement (9). In this case, a slightly higher OCV of 1040 mV was attained. The cell generated a maximum power density of 490 mW/cm² at 1000°C.

In this study electrochemical data of anode supported fuel cells are reported. The cells containing sprayed, ultra-thin electrolytes were operated at 770°C.

EXPERIMENTS

Reducing the electrolyte thickness leads to the electrode supported fuel cell design. We have chosen the anode as support, because compared to the cathode as support, it offers the benefits of lower material cost and better strength. The anode substrates were 300 μm thick disks (35 mm in diameter) containing 8 mol% yttria-stabilized zirconia (YSZ) and nickel oxide (NiO) in the ratio of 30:70 in wt%. The substrate structure had a mean pore size of 1.5 μm with a mean YSZ grain size of 1 μm.

Thin film deposition using the spray pyrolysis involves the spraying of a metal salt solution onto a heated substrate. We have used the spray pyrolysis technique with two different atomizers for the generation of aerosols; either an electrostatic atomizer or an air blast atomizer. Dense films of YSZ electrolyte were deposited by spraying yttrium chloride (YCl₃·6H₂O) (Aldrich Chemicals, Switzerland) and zirconium acetylacetonate (Zr(C₆H₆O₂)₄) (Fluka Chemie, Switzerland) dissolved in an ethanol (C₂H₅OH) (Fluka Chemie, Switzerland) and butyl carbitol (C₈H₁₉O₂) (Fluka Chemie, Switzerland) mixture (50:50 vol.%). The precursor solution was prepared according to the stoichiometry of the required (ZrO₂)_0.92(Y₂O₃)_0.08 film. The overall concentration of salts in the solution was 0.1 mol/l. The precursor solution was atomized to an aerosol by exposing it to either stream of air or high voltage. The deposition temperature was varied from 280°C to 320°C.

The surface morphology and the cross-section of the deposited films were characterized using scanning electron microscopy (SEM) (LEO 1530, Germany).

A cathode layer of La₀.₆Sr₀.₄Co₀.₃Fe₀.₈O₃ (LSCF) of typically 50 μm was finally applied on the electrolyte by screen-printing without subsequent sintering. Ferritic stainless steel plates with gas channels (1.4509 steel: 18%Cr, Nb, Ti) (Plansee AG, Austria) were used as interconnectors. The cell with sprayed electrolyte and screen-printed cathode was then sandwiched between the two interconnects. Platinum wires for voltage and current leads were spot welded on each of the interconnects. The cell with interconnectors was mounted into an alumina housing containing the fuel and air supply tubes and placed in a furnace. The cell was heated up to the working temperature of 770°C at a heating rate of 1°C/min and operated using dry hydrogen as fuel and air as oxidant. The hydrogen fuel flow was varied from 0.1 to 1.8 g/h. Due to the unsealed arrangement rather high hydrogen flows were necessary to obtain the highest OCV values. The air flow was varied from 10 to 50 g/h.
RESULTS

The microstructures of the fuel cells were examined using scanning electron microscopy (SEM). Figure 1 shows the cross-section of a LSCF/YSZ/Ni-YSZ fuel cell structure with a thin YSZ electrolyte prepared by electrostatic spray deposition (ESD) after operating the cell at 770°C for 115 hours using hydrogen as fuel. It was observed that the electrolyte film was uniform, continuous, and adhered well to the anode and to the cathode but had many small pores. The YSZ film thickness varied from 0.5 μm to 1.5 μm. Usually, most of the films deposited by ESD were rougher than those deposited using an air blast atomizer.

Figure 1. Cross-section image of a solid oxide fuel cell with a sprayed electrolyte. From the top to the bottom: screen-printed cathode (LSCF), YSZ electrolyte prepared by electrostatic spray deposition and anode substrate (Ni-YSZ cermet).

Figure 2 shows an SEM image of a solid oxide fuel cell with a sprayed YSZ electrolyte using an air blast atomizer. The cell was operated using hydrogen as fuel at 770°C for 220 hours. The thickness of the electrolyte film was approximately 0.4 μm. As can be seen the film also contained many pores, but in contrast to the one deposited by ESD it was much smoother. The film also appeared to adhere very well to the Ni-YSZ anode. However, this was not the case for the LSCF cathode. The cathode delaminated from the electrolyte because the cell was heated up to the operating temperatures without sintering the cathode.

Figure 3 shows the I-V and I-P characteristics of fuel cells, for which the YSZ film was sprayed using either electrostatic or air blast atomizer. Both cells were operated under similar conditions at 770°C. Air was supplied to the cathode compartment with a flow rate of 25 g/h. Hydrogen gas was supplied to the anode compartment with a flow rate of...
Figure 2. The cross-section of a solid oxide fuel cell with a sprayed electrolyte. From the top to the bottom: screen-printed cathode (LSCF), sprayed YSZ electrolyte using air blast atomizer and anode substrate (Ni-YSZ cermet).

Figure 3. Comparison of fuel cell performances at 770°C. A thin YSZ film was sprayed using either electrostatic (○●) or air blast atomizer (□■) on a NiO/YSZ anode substrate.
0.5 g/h. An open circuit voltage of 880 mV was measured for the cell with the electrolyte deposited using ESD and 970 mV for the cell with the electrolyte sprayed using an air blast atomizer. Due to gas leakage through the YSZ film and unsealed experimental setup, open circuit voltages of the cells were lower than the theoretical value of 1.1 V, calculated from the Nernst equation. This indicates that open porosity can exist in the electrolyte film deposited using ESD. On the other hand, excellent power densities of 450 mW/cm² and 550 mW/cm² were generated. The cells generated a power density at 770°C comparable to the one obtained by Setoguchi et al. at 1000°C (9, 10). It follows that the use of very thin films of YSZ electrolyte allowed us to decrease the operation temperature by 230°C at keeping constant the power output.

The highest OCV achieved using the ESD method producing films of 1 μm thickness was about 880 mV. It is more difficult to deposit gas-tight films when the precursor solution is sprayed by an electrostatic atomizer, because the spray consists of many small droplets. Most of the droplets are smaller than 10 μm. These droplets are almost dry when they get in to contact with the surface of the substrate because small ones evaporate faster than large ones. Therefore, the open pores of the substrate are covered faster with large droplets. Usually, the droplets generated using air blast atomizers are much larger than those obtained using electrostatic atomizers. This explains the higher OCV values of the cells with the electrolyte sprayed using an air blast atomizer.

CONCLUSIONS

In the present paper, we presented and discussed results on anode supported SOFCs with thin electrolytes fabricated by the spray pyrolysis process. Dense and crack-free YSZ electrolyte films were deposited on NiO-YSZ anode substrates. This was demonstrated by the achieved open circuit voltage that was close to the theoretical one. Cells with an YSZ electrolyte layer were prepared using an air blast atomizer exhibited higher OCV, compared to the electrolytes deposited using an electrostatic atomizer. This indicated that higher quality films are obtained using an air blast atomizer. At 770°C an OCV of 970 mV and a power density of 550 mW/cm² were attained. It was observed that a submicrometer thin electrolyte film deposited using the spray pyrolysis could close pores with size of up to 3 μm. We have demonstrated that spray pyrolysis can be successfully applied in SOFC technology as a thin film deposition technique.

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