CELL COMPONENT FABRICATION BY
WET POWDER SPRAYING

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ABSTRACT

Planar, self-supporting SOFCs require thin porous electrode layers of high-
temperature electronic conductors such as La(Sr)MnO₃-perovskite (cathode) and
Ni/YSZ (=Yttria Stabilized Zirconia) cerments (anode). The Wet Powder Spraying
(WPS) is a technique to manufacture these layers. WPS-layers show high homogenity
in thickness, good adhesion to tape-cast YSZ-foils and considerable electrochemical
performance. Also advantageous is the simplicity and speed of WPS-fabrication,
especially to create thin multi-component, very thick (< 1 mm) or graded layers.

INTRODUCTION

Wet Powder Spraying (WPS) is a novel method for the production of porous
ceramic or metallic layers (1). Starting point is a homogenous suspension made of al­
cohol, 2-5 Vol.% of a special organic binder and the ceramic or metallic powder.
While constantly stirring the mixture it is sprayed onto a substrate by compressed air
in an ordinary air-brush pistol (DeVilbiss TGC). The desired shape of the layer is
provided by polyethylene-foils that cover the substrate. The area that is to be coated is
cut into the foils and is thus open to the sprayed suspension. The alcohol evaporates
immediately during the flight of the suspension from the nozzle to the substrate and
leaves a thin, dry layer of the powder, fixed by the binder. The thickness of the layers
can be controlled by particle-size and number of the spraying-cycles. There has not
been found any limitation to shape, size and composition of the powders, but angular
powders < 25 µm show best results in homogenity of the layer-thickness. Directly
after the spraying process the layer and substrate are ready for the heat-treatment.
Further drying is not necessary. The heat-treatment consists of debinding below
400°C (about 1 h) and sintering at elevated temperatures depending on the
composition of the powder. Homogenous layers form with good sticking conditions
and high porosity (20-50 %). The complete process from mixing of the suspension to
the sintered end-product does not take longer than 15 hours.

EXPERIMENTS

PEN's as well as single electrodes for test-purposes were manufactured by WPS.
10-250 µm thick layers of La₀.₈₄Sr₀.₁₆MnO₃ as cathode and Ni or NiO/YSZ in diffe­
rent ratios as anode were sprayed onto sintered YSZ-foils made by tape-casting.
Spraying-parameters (distance nozzle-substrate, spraying-time, alcohol- and binder-
content etc.) as well as grain-size and -shape of the powders were varied to achieve a
porosity of 30-50 %. La₀.₈₄Sr₀.₁₆MnO₃-powders made by nitrate-pyrolysis, spray-
drying and solid-state-reaction were used. Ni or NiO/YSZ-powders made by dry- or
wet-milling and mixing with or without subsequent heat-treatment served as powders for anode-manufacturing. Sintering-conditions, sintering-time, heating-rate and sintering-temperature, as well as shape, weight and composition of bases and covers were varied.

RESULTS

To achieve flat PEN's and YSZ/single-electrode compounds they had to be covered with porous YSZ or CaSZ plates during sintering. The organic compounds of the layers could pass through the covers easily during debinding in the temperature range below 400°C. Variation of the heating-rate between 0.5 and 5 K/min did not change the microstructure of the layers, but too fast heating had a detrimental influence on life of the covers. Although the homogenity of the surface is excellent, it could be improved by using a certain organic dispersant (TPA).

Cathode

Best starting-powder for the cathode was La0.84Sr0.16MnO3, made by solid-state reaction, milled in a ball-mill and sieved < 25 μm. The sintering-temperature of the cathode had to be kept below 1200°C to avoid formation of detrimental phases such as La2Zr2O7 at the interface. By increasing the layer-thickness from 25 μm to 75 μm and use of TPA the performance of the cathode could be improved. Best cathodes showed an overpotential of 200 mV at a current-density of 2 A/cm².

Fig. 1: Sample 1: Powder made by Nitrate-Pyrolysis; 50 μm. Sample 2, 3 & 4: Powder as mentioned in the text; 25, 50 & 75 μm
Anode

For the anode, temperatures > 1300°C are necessary to achieve well adhered layers. There are no reactions at NiO-ZrO₂ interface, so the sintering temperature can be elevated. Segregation of NiO and YSZ during the spraying-process could be stopped by using the organic dispersant TPA and increasing the spraying-distance. Best results showed a two-component layer of fine 1/3 YSZ/NiO (powder < 1 μm) close to the YSZ-foil and an overlaying layer of relative coarse (< 10 μm) pure NiO. This two-component layer was manufactured continously without any intermediate drying- or sintering-step. The maximum current density of the cathode has not been achieved by the anode, but there is a reasonable chance to achieve this by varying powder and spraying-parameter.

Fig. 2: Cross-sections of Sample 4 (left side: cathode; right side: anode)

Fig. 3: Sample 1: NiO/YSZ, 3:1, Powder < 10 μm; segregation of NiO and YSZ; Sample 2 & 3: two-component layer as mentioned in the text, Tₙ = 1300°C & 1500°C
PEN's

PEN's made out of the optimized single-electrodes have not been tested yet. Until now the best PEN's showed power-densities of 180 mW/cm² at 0.5 V (anode: H₂/N₂ 1/4; cathode: O₂; T=950°C). These PEN's have been made out of single-layer anodes of NiO/YSZ with a thickness of 50 μm and 25 μm thick cathodes. The current-density of a cathode of this type is shown in Fig. 1 (Sample 2).

REFERENCES

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