ANODE SUBSTRATES FOR PLANAR SOFC

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ABSTRACT

The objective of the current work is to process graded cermet foils as anode substrates for planar fuel cells. However, because of the complex procedure, the realization might be difficult. The optimization of several processing steps has been initiated. Initial results on material screening are presented and some conceptual studies are reported.

INTRODUCTION

An anode substrate is the mechanical support for a thin electrolyte, usually for an intermediate temperature SOFC PEN element. It serves as gas distributor and current collector on the fuel side of the cell. Furthermore, system requirements like sealing at the edges of the cell and stackability of the PEN must be taken into consideration. As a result, an anode substrate is a complex component. For planar SOFC, it is either a foil or a thin plate with graded porosity along the thickness. A smooth "upper" surface with fine pores in the micrometer range is necessary for the deposition of the electrolyte by thin film technology. On the lower substrate side, a coarse porosity in the millimeter range is needed to allow easy gas penetration. This can be met by a structure with a gradually reduced open porosity. Simultaneously, good electrical conductivity is needed to transport the electrical current through the plate.

A schematic of the HEXIS cell configuration is given in Figure 1. The mechanical support is the metallic interconnector, on which a corrugated sheet is soldered. Since the anode substrate might be fabricated as a self-supporting device by ceramic processing, it may be soldered on top of the corrugated sheet prior to the deposition of the electrolyte.

At EMPA, a project was defined to fabricate anode substrates for planar HEXIS1 PEN elements by water based ceramic powder processing and press forming. The circular cell for HEXIS has an outer diameter of 120 mm and a center bore of 20 mm. Additionally, the anode substrate must be thinner than 1 mm (preferably 0.5 mm).

Because of the very large ratio between lateral dimension and thickness, dry press forming is extremely difficult and not yet practical. Therefore, this is a high-risk project. But striking economical advantages of the method, compared to lamination, spray deposition and other techniques justify the effort. One advantage is the low binder content and therefore a high solid loading in the green state. A second advantage is the possible net shaping of the parts. A third is the large possibility to incorporate pore formers. Last but not least, die pressing is an excellent technique for low cost mass production.
The problems start with the materials and their properties. Which oxide powder mixture leads to optimized properties of the cermet? Which material as a pore former should be added to optimize cermet and should it be granulated together with the cermet, mixed with cermet granules or incorporated while filling the die by metered addition?

It is well known that pressed parts tend to radially crack at the edge and along a tangent line near the center, if precautions are not taken while filling the die. Therefore, a die filling equipment must be designed for the targeted dimensions and the special requirements of the desired graded porosity. Once green bodies are fabricated, the sintering schedule must be optimized and the subsequent steps for PEN production evaluated.

**COMPOSITION OF CERMET**

A substrate may be regarded as composed of two layers from which the upper one of about 30 to 50 μm is the electrochemical active anode and the remaining is the support part. The anode should have a fine distribution of connected nickel particles (after reduction of the NiO) to create a long triple phase boundary. The support should have
good mechanical stability, high electrical conductivity and open porosity to allow gas penetration.

The percolation of nickel through a zirconia matrix is the key issue for the electrical conductivity. The reduction of NiO to Ni with a volume loss of 16% has to be kept in mind for the following ideas. In binary mixtures the percolation threshold varies with the morphology of the grain mixture. For equally sized NiO and zirconia particles the content of NiO must be higher than for a mixture of coarse grain zirconia with fine grain NiO (see figure 2). In the latter case, a portion of very fine zirconia must be added to the mixture as sintering agent. This concept to neck the zirconia component was described by Ekanayake et al. (2) for anodes with 44 up to 65 vol.% NiO. A similar attempt was made by Itho et al. (3) who made mixtures with 40 vol.% Ni in the reduced state and studied the influence of the ratio of coarse to fine grains on the sintering shrinkage, the resultant porosity and the volume loss while reducing the NiO. In both cited papers, round (granulated or agglomerated) coarse zirconia particles were used. Bossel (4) points out in his literature search about anodes, that crushed zirconia satisfies the anode requirements much better than the granulated one. The sharp edges are active sites for sintering and therefore the temperature can be kept low for necking. Also the packing density is lower for crushed material and leads to the desired porosity. These aspects are especially advantageous for the support part of the substrate.

In order to avoid compatibility problems with the 8YSZ thin electrolyte the classical anode material, Ni-8YSZ-cermet, was chosen for the present work. Nevertheless, there is a variety of powder properties of both NiO and zirconia that need to be evaluated.
While a fairly good powder design for an anode can be derived from the literature, little is known for the support. Therefore the work at EMPA is currently focused on the design of powder mixtures for the support. Fifteen different powder qualities were obtained and some of them were mixed, sintered and analyzed in order to find a good compound for necking. Initial results indicate, that the ratio of coarse crushed to fine 8YSZ should be between 5 and 10 and that the NiO content less than 45 vol.% (51 wt.%) in order to get sufficient electrical conductivity in the substrate.

PORE FORMERS

Without pore formers, a maximum of about 40 vol.% fine porosity can be designed by the necking technique and the reduction of NiO to Ni. This is not sufficient for the support part, where the burnout gas and reaction products must be removed and therefore larger additional pores are introduced.

Pore formers are burned out during the sintering schedule and should decompose smoothly in order to generate only a small gas pressure. Fast decomposition, especially at the beginning, leads to crack formation. Pore formers are processed together with the cermet. In the size range of press granules or larger they must be pourable to be either mixed or co-filled into the die together with the granulated cermet. Fine pore formers (in the range of a few microns) are granulated together with the cermet. They must be dispersed in the same slurry as the cermet, since spray drying is the method chosen for granulation.

The evaluated pore former materials were separated into two groups, namely carbon in form of graphite and carbon black and polymers. Both are available in sizes between several nanometers up to millimeter. The decomposition temperatures were measured by thermogravimetry in air and all decomposed completely below 650 °C. A challenging problem to be solved is to disperse fine carbon in water to mix it with the cermet.

The evaluated polymers as pore formers included fibers like cotton, wool, cellulose and polypropylene and granular powders like wood dust, wax, polycrylicate and PVA. Other organic materials with oriented structure were studied in order to incorporate oriented porosity into the support part of the substrate.

DIE FILLING DEVICE

The key to successfully press plates of small thicknesses is a die-filling device that guarantees a very homogenous distribution of powder across the die. Nowadays available equipment is only usable for parts with a thickness of more than several millimeters at the needed lateral dimensions. Therefore, screen type or sonically assisted dosing systems have to be considered and designed. To die press a graded microstructure either graded dosing or multiple step pressing is envisaged.
SUMMARY

In the framework of the development of intermediate temperature SOFC, a project was defined to make a contribution to anode substrate fabrication for planar cells on the basis of classical electrolyte and electrode materials. The fabrication methods include die pressing, lamination of slurry cast foils for the support part and wet spraying or screen printing for the top anode layer in order to get a graded structure of the substrate. Cost consideration and scale up procedure led to the decision to use water based slurries only. Current work is focussed on the optimization of cermet mixture, evaluation of pore formers, suitable lubricants and on the design of dies, filling device and other fabrication aids in this challenging project.

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