STATUS OF SOFC COMPONENT DEVELOPMENT AT ECN

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ABSTRACT

The influence of the electrode microstructure and the manufacturing technique on the cell performance has been determined. For the anode cermets the influence of the Ni- and zirconia particle size has been investigated as a function of pre-calcination temperature of zirconia and of the sintering temperature of the final cermet on the electrolyte. Anodes with the lowest sintering shrinkage show the best performance. For the cathode, the powder processing has been optimized, in order to obtain an optimum cathode/electrolyte interface with high cathode particle loading. The fabrication of the cell structures has been improved and made more efficient by means of co-firing the electrodes on the sintered electrolyte.

INTRODUCTION

ECN is developing flat-plate concept SOFC since 1989 (1,2,3,4). The research programme is carried out in direct cooperation with Siemens AG (Germany) and funding is partly obtained in two CEC sponsored programmes, i.e. JOULE and BRITE/EURAM. Much of the work of ECN has been state-of-the-art material- and component development, in order to obtain cells with high performance. In addition, manufacturing techniques have been developed for upscaled (10 x 10 cm²) cells, using tape casting. The optimized and upscaled cells will be applied in the flat-plate or "multiple array" reactor concept of Siemens, using a metal separator plate. More recently, ECN also has started a materials development programme for low temperature SOFC operation. New results for the optimization of state-of-the-art SOFC electrode materials and for the manufacturing of upscaled cells will be presented in this paper.

COMPONENT DEVELOPMENT

Anode development

State-of-the-art anodes for operation at conventional temperatures (900–
1000°C) consist of Ni/8 mol% Y₂O₃-stabilized ZrO₂ (8YSZ)-cermets. At ECN, standard anode cermets contain 55 vol% Ni in 8YSZ after reduction. For the fabrication of the cermets, commercially obtained NiO powder and pre-calcined 8YSZ are ball-milled in acetone. Subsequently, a suspension of this powder-mix is tape cast onto the sintered electrolyte and the anode is fired on the electrolyte in air. Reduction of the anode occurs during cell operation. The pre-calcination temperature (Tₚₖ) of 8YSZ and the sintering temperature (Tₛ) of the final anode cermet on the electrolyte have systematically been investigated, in order to optimize the microstructure in terms of 1/ high lateral conductivity, 2/ low anode voltage losses and 3/ low sintering shrinkage. Table 1 shows the median particle sizes (D50-values) of NiO and 8YSZ after ball-milling. For 8YSZ different Tₚₖ's have been investigated.

Table 1. Median particle size of NiO and 8YSZ after ball milling. Tₚₖ = pre-calcination temperature (°C) of 8YSZ.

| Tₚₖ in °C | D50 (μm) |
|-----------|----------|
| - (powder as received) | < 1 |
| 1250 | 3.1 |
| 1400 | 6.6 |
| 1550 | 11.6 |
| NiO | 1–2 |

The lateral conductivity of the tape cast anode cermets was measured at 950°C, using a four-probe method (5). The results of the measurements are given in Table 2 for different combinations of Tₚₖ and Tₛ. Table 2 shows that pre-calcination is a pre-requisite for electrical conductivity, whereas the sintering temperature of the anode should be lower than 1500°C. In order to obtain lateral electronic conductivity, it seems necessary to use YSZ-particles with a median particle size larger than 1 μm (see table 1). This phenomenon can be explained by means of the percolation theory, as applied to the electrical conductivity of composites (6). It can be concluded, that the powder particle dimension ratio 8YSZ/Ni must at least be higher than 1, in order to obtain electrical conductivity. Table 2 also shows that the lateral conductivity depends upon the sintering temperature Tₛ. Above 1400°C there is no lateral conductivity. This can be explained by the fact that an increasing sintering temperature is accompanied with a growth of NiO-particles, which also results in larger Ni-particles after reduction of the anode, i.e. powder particle ratio 8YSZ/Ni is decreasing and hence, the lateral conductivity disappears. The growth of the NiO-particles as a function of Tₛ is clearly shown in Figure 1.
Figure 1. Microstructure of reduced anode cermets (55 vol.% Ni in 8YSZ). $T_p$ of 8YSZ in both cases was 1400°C. $T_s$ was 1300°C for the upper photograph and 1500°C for the lower photograph respectively.
Table 2. Influence of $T_{PC}$ and $T_s$ on lateral conductivity of tape cast anodes.
  $+$ = lateral conductivity occurs, which for all samples is in the order of 1000 S/cm, $-$ = no lateral conductivity measured.

| $T_{PC}$\$T_s$ | 1200 | 1300 | 1400 | 1500 |
|----------------|------|------|------|------|
| $-$ as received | $-$  | $-$  | $-$  | $-$  |
| 1250           | $+/-$| $+$  | $+$  | $-$  |
| 1400           | $+$  | $+$  | $+$  | $-$  |
| 1550           | $+$  | $+$  | $+$  | $-$  |

The effect of $T_{PC}$ and $T_s$ on the anode potential has also been determined by means of a three electrode method. With this method the voltage losses over the anode (3 cm$^2$ active electrode area), at a current density of 100mA/cm$^2$ and an operation temperature of 930°C were determined. The results are shown in table 3. From this table it can be concluded that the highest $T_{PC}$ for 8YSZ and the lowest $T_s$ results in an anode with the lowest electrode voltage loss. In practice, such an anode is characterized by the lowest shrinkage behaviour during manufacturing.

Table 3. Voltage losses over the anode in mV with $I=100$mA/cm$^2$ and $T = 930^\circ$C.

| $T_{PC}$/$T_s$ ($^\circ$C) | 1200 | 1300 | 1400 |
|---------------------------|------|------|------|
| 1250                      | 570  | 2520 | $--$ |
| 1400                      | 370  | 294  | 303  |
| 1500                      | 240  | 321  | 411  |

With the same three electrode method, also electrode/electrolyte interface impedances have been obtained, with a Solartron 1255 frequency reponse analyzer. From the impedance data it is possible to obtain the electrolyte surface area, which is covered by active anode–sites. The contribution of the electrode impedance and the electrolyte impedance can be separated in the impedance spectrum. In general, the measured value of the electrolyte resistance $R(B)$ is not similar to the expected (theoretical) value for the electrolyte resistance. This can be attributed to the fact, that a small part of the electrolyte surface is contributing to the conductivity i.e. only the part which is covered by Ni–particles from the anode microstructure. This apparent or active surface can be calculated by the formula
A = \rho_B * T_B / R_B \quad [1]

where A = active surface, T_B = thickness of electrolyte, R_B = measured electrolyte resistance and \rho_B = specific resistance of the electrolyte at 930°C. In Table 4 the A-values (as a fraction of the total electrolyte area) are given as a function of T_{PC} and T_S. The A-values are a measure for the amount of active sites on the anode/electrolyte interface. It can be concluded from Table 4 that the best performing anodes (see Table 3) also have the highest A-values.

Table 4. Apparent or active electrolyte surface as a fraction of total electrolyte area (calculated from formula [1]). See text for explanation.

| T_{PC}/T_S (°C) | 1200 | 1300 | 1400 |
|----------------|------|------|------|
| 1250           | 7.3  | 1.1  | --   |
| 1400           | 23.5 | 20.3 | 14.8 |
| 1500           | 27.5 | 12.5 | 4.3  |

Cathode development

At ECN, state-of-the-art cathodes for operation at conventional temperatures (900–1000°C) consist of a porous structure of La_{0.85}Sr_{0.15}MnO_{3-x}. The cathode powder is made by citrate pyrolysis (1). After calcination and milling, the powder is suspended in the binder system and tape cast on the sintered electrolyte. The cathode is fired on the electrolyte at temperatures < 1300°C in air. For optimization of the microstructure, powder morphology modification and sintering temperature of the cathode on the electrolyte have been investigated. The objectives of the optimization process were: 1/ optimum three-phase boundaries at the electrolyte/cathode interface and 2/ optimum adhesion of the cathode to the electrolyte.

By changing the pre-calcination and milling steps of the pre-cursory cathode powder, a range of cathode microstructures could be obtained. In Table 5 the voltage losses over the cathode are given as a function of microstructure characteristics. Powder I is a well-defined cathode powder with no agglomerates, which results in a homogeneous microstructure after tape casting. Powders II and III are subsequently more agglomerated. The most prominent difference between the resulting microstructures is the occurrence of larger macro-pores, which result in relatively high cathode losses. The micro-pores between primary cathode
Table 5. Voltage losses (mV) over the cathode (i = 100 mA/cm²) at 930°C, as a function of electrode microstructure.

| Powder code | I   | II   | III  |
|-------------|-----|------|------|
| Cathode losses (mV) | <75 | 100–150 | >200 |
| Micro-pores (μm) | 0.2–1 | 0.2–1 | 0.2–1 |
| Macro-pores (μm) | <1.5 | 2–5  | 2–10 |

crystallites are similar for all three micro-structures. It is concluded that a high cathode particle loading on the electrolyte/cathode interface is beneficial for the cell performance. A more open microstructure (powders II and III) is favoured for the cathode structure adjacent to the interface layer, in order to guarantee gas-diffusion and electronic conductivity.

Apart from a high cathode particle loading on the cathode/electrolyte interface, also an optimum adhesion of the cathode structure to the electrolyte is required. Adhesion has been optimized by investigating the sintering temperature of the cathode to the electrolyte and by minimizing the cathode shrinkage during firing. At sintering temperatures below 1200°C no densification of the cathode microstructure is observed. Only neck-growth between adjacent cathode particles and between the cathode and the electrolyte occurs. A positive correlation is observed between sintering temperature and adhesion of the cathode structure to the electrolyte. No secondary phases could be detected with SEM or XRD on the electrolyte/cathode interface, even at the highest sintering temperatures. The sintering shrinkage of the cathode has been decreased by increasing the green density of the cathode structure and by pre-calcining the cathode powder at 1400°C. The effects of powder morphology, sintering temperature and degree of sintering shrinkage are currently under investigation with the above mentioned three-electrode configuration, in order to obtain more information about cathode voltage loss and impedance data.

MANUFACTURING TECHNIQUES

In the past (3), a three step procedure was developed for the fabrication of the cells. In a first step, the electrolyte was tape cast and sintered in air at 1500°C. The resulting electrolyte thickness was 130 μm. After tape casting and firing of the anode on the sintered electrolyte (1300°C in air), the cathode was tape cast...
and sintered on the electrolyte (1100°C in air). Now, for reasons of efficiency, both the optimized electrodes structures are tape cast on the sintered electrolyte and are co-fired at 1200°C. As can be seen from Tables 3 and 4, this firing temperature results in optimum anode performance. For the cathode, the sintering temperature is higher as was used before (1100°C), which results in a better adherence to the electrolyte. By using the optimized cathode powder morphology, a high cathode powder particle loading on the interface with the electrolyte could be realized, which results in low cathode voltage losses (see Table 5).

In addition, upscaling of the dimensions of sintered electrolytes (8YSZ) has resulted in maximum sizes of 20x20 cm². Maximum dimensions of cells, which have been made with the above described "co-firing" technique, were 15x15 cm² electrolytes with 14x14 cm² electrode areas. Thickness of the electrolytes in all cases is 130μm.

CELL-TESTING

Cell tests have been performed with PEN-structures with optimized anode- and cathode-structures, which were co-fired on the sintered electrolyte. Electrolyte dimensions for these materials tests were 5 x 5 cm² with an active electrode area of 11 cm². Fig. 2 shows the cell performance of such a cell. The anode (55 vol% Ni in 8YSZ) contains 8YSZ which was pre-calcined at 1500°C. The anode gas was hydrogen (500 ml/min), which was humidified at room temperature. The cathode is an optimized structure of La₉₃Sf₀₁₅MnO₃_x which was tested under air and under pure oxygen (both 500 ml/min) (see Fig. 2). For current collection, Pt-grids were used.

CONCLUSIONS

Both anode and cathode microstructures could be optimized by systematically changing the processing parameters. For the anode-cermet an optimum pre-calcination temperature of 8YSZ and an optimum firing temperature of the anode on the sintered electrolyte could be determined. In fact, the anodes with the lowest sintering shrinkage under oxidizing conditions, show the best performances. For the cathode, a large amount of 3-phase boundaries at the electrolyte/cathode interface is a pre-requisite for a good cell performance.

The optimized electrode structures could be co-fired on sintered electrolytes of < 15 x 15 cm² with a thickness of 130 μm. Cells with electrolytes of 5 x 5 cm², under ideal operating conditions, yielded 0.4 W/cm² at a cell voltage of 0.7 V.
Figure 2. Voltage–current characteristic of a single cell of 5x5 cm$^2$. For testing conditions see the text.

**ACKNOWLEDGEMENTS**

Financial support from the CEC (Contracts JOUE–048–C and BREU–CT91–0423) is gratefully acknowledged.

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