ABSTRACT

Improved materials are needed to lower the operating temperature of the SOFC, which in parallel opens up the possibility of reducing manufacturing costs. In this context, variation of the oxide component of the anode substrate was investigated by substituting 8YSZ (8 mol% Y$_2$O$_3$ stabilised ZrO$_2$) by TiO$_2$ or Al$_2$O$_3$. A low-cost production route involving tape casting for substrate manufacture was shown to be suitable and thinner electrolytes (~4µm) with sufficient gas tightness. Some suitable cathode materials are also presented. In order to reduce manufacturing costs, a new interconnect material based on ferritic steel for low-temperature operating conditions and a new casing design for stack testing was introduced. To investigate the corrosion and interfacial scales more precisely, complete stacks were prepared for metallographic post-mortem analysis.

INTRODUCTION

The anode supported planar SOFC concept has been designed and tested at Forschungszentrum Jülich (FZJ) [1 and references therein]. A thin electrolyte of about 15 µm is deposited on thick (1 - 2 mm) anode substrates (see Figure 1). The thin electrolyte

![Figure 1. Schematic cross-section of a SOFC cell (FZJ-design); the dimensions of the layers are not true to scale.](image-url)
film allows operation at lower temperatures due to reducing the ohmic losses of the electrolyte and also lowers the costs of the interconnect and casing materials of the stack. The standard materials which are used for the cell components and stacks are listed in Table 1.

Table 1. Materials and thicknesses of the components used in the standard anode supported concept.

| Component                                | Material                                      | Thickness |
|------------------------------------------|-----------------------------------------------|-----------|
| interconnect with gas channels           | X10CrAl18 / 1.4742                            | 2000 µm   |
| anode contact layer                       | nickel mesh                                   | ~ 250 µm  |
| substrate (anode)                         | NiO + 8YSZ                                    | 1500 µm   |
| anode functional layer                    | NiO + 8YSZ                                    | 5 µm      |
| electrolyte                               | 8YSZ                                          | 15 µm     |
| cathode intermediate layer                | La₀.₆₅Sr₀.₃₀MnO₃ + 8YSZ                       | 10 µm     |
| cathode                                  | La₀.₆₅Sr₀.₃₀MnO₃                             | 40 µm     |
| cathode contact layer                     | LaCoO₃                                        | ~ 75 µm   |

New materials and processing techniques for all the cell and stack components are looked for to improve reliability and cost. Therefore, anode substrates based on Ni/TiO₂ and Ni/Al₂O₃ cermets are fabricated with the aim of adjusting the TECsubstrate to the TECelectrolyte. For cost reduction, the tape casting process for manufacturing planar substrates (FZJ-design) could substitute the CoatMix™ process. Very similar values for properties like gas permeability, electrical conductivity and porosity have to be achieved.

In order to lower the operating temperature, investigations are being performed on improved materials for the cathode, contact layers and interconnect. The cathode material La₀.₆₅Sr₀.₃₀MnO₃ (LSM) is presented with variations in the praseodymium, iron and cobalt content. For interconnect materials, corrosion tests show that ferritic steels with special additions could be possible candidates and will considerably reduce costs. For the same reasons, a new casing design was introduced. To investigate the corrosion and interfacial scales more precisely, complete stacks can be prepared for metallographic post-mortem analysis, for which purpose the stack will be infiltrated with a resin and after polymerisation cut into slices using a water jet.

NEW MATERIALS AND COMPONENTS FOR MANUFACTURING

SUBSTRATE

Eliminating the mismatch between the thermal expansion coefficients of the substrate and the electrolyte and reducing the cost of the substrate (normally Ni/8YSZ) are necessary for a successful introduction of a future SOFC. The mixture of nickel (40vol%) and 8YSZ (60vol%) has a TEC of around $\alpha = 12.6 \times 10^{-6} \text{ K}^{-1}$ and shows a mismatch to the TEC of 8YSZ with $\alpha = 10.6-11.1 \times 10^{-6} \text{ K}^{-1}$ [2, 3]. Oxides like Al₂O₃ and TiO₂ have a smaller TEC than 8YSZ and in addition are cheaper. Moreover, it is possible to adjust the
thermal expansion behaviour of these oxides to other cell materials (i.e. membrane material - 8YSZ or interconnect materials - ferritic steel or LaCrO₃). Calculations of the TEC of the Ni/Al₂O₃ cermet and the Ni/TiO₂ cermet depend on the nickel content and are shown in Figure 2.

Taking into account the reduction behaviour, gas permeability and electrical conductivity [3], Ni/TiO₂ (40vol% Ni) was selected as a possible substitute for Ni/8YSZ. All the parameters mentioned above are superior to the standard Ni/8YSZ substrate. In the case of Ni/Al₂O₃ substrates (40 and 60 vol% Ni), a reduction temperature of 1373 K is needed in contrast to 1173 K for NiTiO₃, because of the higher thermal stability of NiAl₂O₄. Also a lower electrical conductivity was recorded for the Ni/Al₂O₃ cermet. This fact is due to low sinterability and the resulting highly porous microstructure and the missing electrical pathways in the cermet.

![Figure 2. Calculated (lines) and experimentally determined (symbols) TECs of porous cermets made by the CoatMix® process depend on the Ni fraction after reduction. Legend: (............) Ni/TiO₂ cermets, (............) Ni/Al₂O₃ cermets, (------------) Ni/8YSZ cermets, | | TECYSZ [3].](image)

For cost reduction the substrates can be produced by a conventional low-cost tape casting process instead of applying the standard CoatMix® process. The tape casting slurry is based on organic solvent and fine graphite powder as a combustible component in combination with a mixture of coarse and fine YSZ powder and NiO powder. The powder mixture was stabilised in ethanol / toluene by using a polycondensed fatty acid as a dispersant and a PVB-BBP mixture (polyvinyl butyral – benzyl butyl phthalate) as binder. To retain a short drying time, a 0.6 mm thick green tape was applied to the silicon-coated polymer carrier. After cutting, laminating up to 1.2 mm and sintering, the tapes show a high gas permeability of > 0.04 x 10⁻⁹ cm², a bending strength of ~ 80 MPa, an average pore diameter of 1.5 μm and an electrical conductivity of 750 S/cm at 1173 K.
The electrochemical performance shows power densities of > 200 mW/cm² at 750°C (see Figure 3). This performance is as good as of cells which were manufactured by the CoatMix® process and demonstrates the usability of the tape casting process for manufacturing SOFC substrates [4].

![Current-voltage characteristics of a cell with a tape cast substrate (effective area 40x40 mm²) in humidified hydrogen and air (other components see Table 1).](image)

**Figure 3.** Current-voltage characteristics of a cell with a tape cast substrate (effective area 40x40 mm²) in humidified hydrogen and air (other components see Table 1).

**ELECTROLYTE**

To lower the temperature of the SOFC, a thin gas-tight electrolyte film (8YSZ) reduces the resistance of the electrolyte and allows operation below 1073 K. Thicknesses ranging from 5 to 50 µm are obtainable if 8YSZ is deposited by vacuum slurry coating (VSC®), [1]. A new two-step processing, i.e. primary coating and firing followed by secondary coating and sintering, makes it possible to manufacture thicknesses of around 4 µm with the same gas-tightness as a comparable one-step coating with 15 µm thickness. Typical leakage rates of these thin two-step process electrolytes are lower than 1 x 10⁻⁴ mbar l s⁻¹ cm⁻².

**CATHODE**

The detailed production and application processes of the standard cathode material (La₀·₆₅Sr₀·₃ₒMnO₃ = LSM) are published elsewhere [5]. The optimisation of the cathode materials for use at lower temperatures requires an increase in the catalytic activity and a better adjustment of the TEC cathode while retaining electrical conductivity and chemical compatibility (especially by avoiding the formation of La₂Zr₂O₇). It can be postulated that...
an increase of the strontium content increases the catalytic activity. But at the same time strontium increases the TEC cathode and decreases the chemical compatibility. Elements like praseodymium compensate these effects [2, 7, 8]. For an improved electrical conductivity LSM with cobalt, and for mixed conductivity with iron, on B-position were prepared and measured [9]. Therefore different materials with a composition of \( \text{La}_{0.95-x}\text{Sr}_x\text{M}_{1-y}\text{Co}_y\text{O}_3 \) where \( \text{Ln} = \) lanthanum or praseodymium and \( \text{M} = \) manganese or iron were tested (see Table 2). \( \text{V(I)} \)-characteristics were measured before and after annealing at 1073 K and 300 mA/cm\(^2\) for 120 hours (Figure 4). Cobalt and praseodymium perovskites show a better electrochemical performance than the standard cathode material LSM (see Figures 5 and 6). The performance of the ferritic cathode material \( \text{La}_{0.75}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3 \) is not as good as the standard LSM. A possible reason could be the higher sinterability of this materials which leads to a higher density. Investigations on the microstructures of the tested cells will clarify this question.

The effects of rare earth metals can probably be further enhanced by using perovskites containing neodymium, samarium, europium or/and gadolinium, which will be investigated next.

![Figure 4. V(t) of the performance of the Pr\(_{0.65}\text{Sr}_{0.30}\text{MnO}_3\) cathode cell with a load of 300 mA/cm\(^2\) (effective area 40x40 mm\(^2\)) for humidified hydrogen and air include the recording of two \( \text{V(I)} \)-characteristics (measurements 1 and 2).](image)
Table 2. Cathode materials for adjusting the TEC<sub>cathode</sub> and chemical compatibility.

| material               | thermal expansion coefficient (TEC)* | aim of investigation                                                                 |
|------------------------|--------------------------------------|--------------------------------------------------------------------------------------|
| La<sub>0.65</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> | 12.3 x 10<sup>-6</sup> K<sup>-1</sup> | standard material                                                                    |
| Pr<sub>0.65</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> | 11.6 x 10<sup>-6</sup> K<sup>-1</sup> | influence of praseodymium, cobalt and iron on the electrochemical performance, TEC and chemical compatibility (formation of Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>) |
| La<sub>0.75</sub>Sr<sub>0.2</sub>Mn<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> | ---                                 |                                                                                      |
| Pr<sub>0.75</sub>Sr<sub>0.2</sub>Mn<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> | 10.6 x 10<sup>-6</sup> K<sup>-1</sup> |                                                                                      |
| La<sub>0.75</sub>Sr<sub>0.2</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> | 14.8 x 10<sup>-6</sup> K<sup>-1</sup> |                                                                                      |

*TEC<sub>YSZ</sub> is 10.8 x 10<sup>-6</sup> K<sup>-1</sup>*

Figure 5. Current-voltage characteristics of different cells (effective area 40x40 mm<sup>2</sup>) for humidified hydrogen and air at 1073 K.
INTERCONNECT

Because of the low operating temperature between 973 and 1173 K, a ferritic steel can in principle be used as an interconnect material. This alternative will considerably reduce the cost in comparison to an ODS alloy (Cr5Fe1Y2O3). The thermal expansion coefficient (TEC) of ferritic steels with additions of chromium between 10 and 30 % are close to the TEC of the Ni/8YSZ-anode substrate (TEC = 12.5 $10^{-6}$K$^{-1}$). Additionally, other properties like corrosion resistance in oxidising and in reducing atmosphere, chemical compatibility with the contact layers and an acceptably low ohmic resistance of the oxide layer formed during stack operation have to be taken into account. Alloys with $\sim 13-18$ $\%$ chromium and $\sim 1$ $\%$ Al have a high oxidation resistance. The formation of electrically insulating Al-oxides layers is suppressed by surface treatments like sandblasting but in that case local formation of (Fe,Cr)$_2$O$_3$ can result in high corrosion rates. Ferritic steels with around 24% chromium doped with low contents of metals like Y and Mn show a high oxidation resistance due to the formation of adherent surface layers. Detailed measurements are described in [10].

CONTACT LAYERS

Figure 1 shows the contact layers which are necessary to provide the low resistive electrical contacts between the interconnect and the electrodes in the stack. On the fuel
The contact layer is formed by a nickel mesh which is welded to the interconnect. Detailed examinations regarding the catalytic activity of the anode contact layer, the nickel mesh, in comparison with the catalytic properties of the anode substrate have been published elsewhere. On the oxidant side (cathode) a LaCoO₃ paste is usually applied to the ribs of the interconnect. In order to improve the cathode contact layer several substitute perovskites based on LaCoO₃, LaFeO₃, and LaMnO₃ were tested with respect to their electrical conductivity, their thermal expansion coefficient and their compatibility with the cathode and the interconnect [11]. The best combination of properties was found for strontium-doped LaMnO₃ (LSM), which is identical to the cathode composition. LSM powder prepared by the “urea process” starts sintering at 700°C due to its low crystallite size of 30-40 nm resulting in a good electrical contact between interconnect and the cathode.

MANIFOLD DESIGN, SEALING, CASING OF THE STACK AND POST-MORTEM ANALYSIS

Failure analysis of stacks involves cutting stacks into slices after operation. This destroys all stack components. A simpler and cost-effective casing is required to obtain sufficient number of specimens for analysis [12].

The material used for interconnects and casings is a commercially available ferritic chromium steel. The new design consists basically of three parts, a ring and two plates as base plate and top plate, as shown in Figure 7. The external manifold, i.e. the gas chambers, are constituted by the ring, which is precisely machined by water jet cutting from a 20 mm thick plate in a single process. The base plate which contains connectors to

Figure 7. New casing design consists of three parts, a ring, base plate and top plate for a short stack, 250 x 250 mm².
the tubes for the gas supply is vacuum-brazed to the ring. This casing is then preglazed with a type of sealing glass in order to achieve electrical insulation. A layer of 0.1 mm of crystallized glass ceramic is necessary to prevent short circuit between casing and interconnects or anode supported cells. After this preglazing the casing is used as a fixture for the stacking process. The interconnects and cells fit into the casing, so that only narrow gaps between the edges of the stack and the casing must be sealed afterwards.

Contact layers are incorporated in order to level out tolerances. On the cathode side a paste of perovskite powder (LaCoO$_3$, LaSrMnO$_3$) is used, on the anode side a nickel mesh is spot welded to the interconnect. An alkali-free glass ceramic system is used for sealing, which has a high thermal expansion coefficient of $12 \times 10^{-6}$ K$^{-1}$ and was tuned for optimum flow and sintering behaviour under the boundary conditions for stack sealing. The glass ceramic is applied as a paste as well. The stacking process involves application of a pressure of more than 300 kg for a 100 x 100 mm$^2$ stack (≈ 0.3 MPa), to get thin and uniform contact layers.

After operation the whole stack with casing is infiltrated with epoxy resin and cut into slices using a water jet. This type of dismantling induces no harmful mechanical loads on the stack and therefore permits the investigation of stacks in an in-situ condition and especially the examination of contact layers, which seem to have a predominant effect on degradation, Fig. 8.

![SEM photograph of a cross-section of epoxy resin infiltrated stack (bipolar plates, two cells and contact layers) which was cut into slices by a water jet.](image)

**Figure 8.** SEM photograph of a cross-section of epoxy resin infiltrated stack (bipolar plates, two cells and contact layers) which was cut into slices by a water jet.

**SUMMARY**

The lowering of the operating temperature allows, on one hand, cheaper materials and manufacturing processes to be used for cell and stack components like the substrate, cathode, interconnect and casing. On the other hand, this requires materials with
improved properties in the area of catalytic activity and electrical and ionic conductivity. Such materials are presented here. Investigations for adjusting the TECs are still necessary.

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