INVESTIGATION OF POROUS METALLIC SUBSTRATES FOR PLASMA SPRAYED THIN-FILM SOFCs

Thomas Franco, Zeynep Ilhan, Michael Lang, Günter Schiller and Patrice Szabo
German Aerospace Center (DLR)
Institute of Technical Thermodynamics
Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany

ABSTRACT

In a novel auxiliary power unit (APU) stack concept for on-board electricity generation in vehicles and aircraft, a porous metallic substrate for cell support is used. In the plasma sprayed DLR SOFC concept, the substrate has to fulfil a variety of required properties. A combination of all these requirements in an integral substrate structure has turned out to be a key problem in this novel design. Therefore, together with some partners a substrate development process has been established. This paper focuses on different substrates developed at DLR and on the investigation methods that are used for it. Furthermore, it shows some results of gas permeability and leakage tests and of electrical and electrochemical characterisations under SOFC-relevant conditions that were carried out by means of the four-point measurement technique.

INTRODUCTION

To manufacture very thin and stable electrodes and electrolyte layers, a porous metallic substrate structure for cell support is essential for the planar DLR SOFC concept. In this concept the entire MEA (Membrane-Electrode-Assembly) is deposited onto a porous metallic substrate by an integrated multistep vacuum plasma spray (VPS) process (1). The principle of this concept is schematically shown in Fig. 1 and has been described in detail elsewhere (2, 3).

In the first generation stack, the substrate supported cells were generally fitted into a frame between machined ferritic steel interconnect plates and sealed by a glass sealant layer that typically consists of alkaline earth borosilicate glass (4, 5). In general, the metallic housing was simple with relatively thick bipolar plates and hence mainly aimed at stationary applications. In contrast, for mobile application to be used as an auxiliary power unit (APU) for on-board electricity generation in vehicles (6) and aircraft, a second generation stack design has become essential. Within a consortium led by BMW AG, the conventional DLR stack design has been modified to meet the very strict requirements for reduced volume and weight. This results in a new stack design for APU application that is based on thin stamped metal sheets which can be laser welded to form a metallic bipolar cassette with integrated brazed substrate-cell compound. Fig. 2 shows a 3-D view of such a novel APU stack design.
Previous work (5, 7) showed that the porous metallic substrate is an essential key component. The stack operating conditions are highly demanding on the metallic substrate structure. Thus, it has to fulfil a variety of required properties, e.g. high electrical conductivity, adequate corrosion stability in SOFC-relevant atmospheres and an adapted thermal expansion coefficient (~ 11 x 10^-6 K^-1, 30 - 1000°C) with respect to the MEA. Furthermore, some structural properties have to be added like a high gas permeability (porosity ~ 50 vol% and higher) for a sufficient fuel gas supply to the anode, mechanical strength for cell support and a thin (200-300 µm) and fine porous top layer (pore size distribution -50+5 µm) to deposit planar and closed MEAs. A combination of all these requirements in one integral substrate structure has turned out to be a key problem in the APU stack design.
SUBSTRATE DEVELOPMENT

The structural requirements especially necessitate a separate substrate development process with respect to the plasma spray cell fabrication and to the APU stack integration. Over the years some substrate structures have been developed and adapted to the VPS concept together with different partners from industry. Table 1 shows an overview of all porous metallic substrates used for cell support at DLR. The fabrication process and the assembly of these substrate structures have been described in detail elsewhere (5, 7, 8).

Table 1. Porous metallic substrates used for cell support at DLR.

| Substrate                  | Material                        | Thickness / [mm] | Porosity / [vol%] | Supplier/Partner                           |
|----------------------------|---------------------------------|------------------|-------------------|--------------------------------------------|
| Fibre Felts                | Ni and/or Fe-22Cr-5Al-0.1Y       | ~1.8             | >85               | Bekaert, Belgium/Technetics, USA            |
| Woven Wire Structures      | Crofer22APU                      | ~1               | ~60               | Rhodius, Germany/Haver&Boecker, Germany    |
| Knitted Wire Structure     | Crofer22APU                      | ~1               | ~35               | Rhodius, Germany                           |
| Sintered Porous Metal Plate| Fe-26Cr-(Mo,Ti,Mn,Y2O3), (TM 14) | ~1               | ~50               | Plansee, Austria                           |

The successful utilisation of these substrate materials in a novel SOFC APU design for cell support requires more knowledge about the structural and material characteristics of the substrates during SOFC-relevant operation conditions. Therefore, some special studies were performed at DLR.

SUBSTRATE INVESTIGATION METHODS

Concerning the material characteristics, several methods were used at DLR in order to investigate and test different substrate materials under SOFC-relevant conditions. These are e.g. 4-point measurements in the model atmosphere Ar-5% H2-3% H2O to investigate electrical conductivity and contact resistance, annealing tests in H2-50% H2O atmosphere and simulated reformate gas like H2/N2-H2O at 800°C to investigate the oxidation stability, and dilatometer measurements (DIL 402 C, Netzsch, Selb) in the temperature range 30-1000°C in Ar-5% H2 atmosphere to investigate the thermal expansion behaviour. Post-investigations were generally made both by optical (OM) and scanning electron microscopy (SEM/EDX) and by X-ray diffraction (XRD).

To investigate the structural characteristics, methods like quantitative image analysis (QIA) and Hg-porosimetry were used to determine porosity. Furthermore, some permeability tests and leak rate measurements on substrate supported electrolytes were carried out. Finally, to investigate substrates under SOFC-operating conditions electrochemical cell tests were carried out to determine I-V characteristics and impedance spectra.
RESULTS AND DISCUSSION

Material and Structural Investigations

A high specific electrical conductivity of the porous metallic substrates is necessary for an adequate cell performance. Fig. 3 shows the temperature dependency of the specific electrical conductivity of investigated porous metallic substrates in simulated model gas atmosphere Ar-5% H₂-3% H₂O. The comparison includes the high porosities of the substrate materials (Table 1).

As expected for metals, the electrical conductivity decreases with increase in temperature. In spite of the high porosity, the nickel felt (> 85 vol%) shows with 2.4 x 10⁻⁵ S/m at 800°C a conductivity that is more than half an order of magnitude higher than the FeCrAlY felt with the same porosity. In accordance with reference (9), bulk nickel shows a significantly higher electrical conductivity than conventional bulk ferritic steel alloys.

In contrast, woven Crofer22APU wire structure shows a conductivity of 1.4 x 10⁻⁵ S/m at 800°C that is significantly higher than the conductivity of 7.4 x 10⁻⁴ S/m of the Crofer22APU knit fabric structure, in spite of the higher porosity of the woven wire structure (Table 1). This effect is attributed to the structural assembly of the Crofer22APU substrates. The 4-point technique measures only the conductivity in a lateral direction and not in a transverse direction. Thus, the lateral conductivity is predominantly influenced by the structure direction of the woven wires.

Furthermore, it is remarkable that the novel Plansee ITM 14 substrate that is fabricated as a powder metallurgical sintered plate (10) possesses nearly the same conductivity as the...
Crofer22APU knit fabric structure. This means that the higher porosity of the Plansee alloy (Table 1) has no significant influence on the conductivity. The conductivity is mainly influenced by the alloy characteristic itself.

Besides electrical conductivity, the substrate porosity influences directly the gas distribution and the release of reaction products on the anode side as well as the thermomechanical cell stability. Especially in the case of substrates consisting of felt materials, cell degradation processes during cell operation can occur that are mainly attributed to subsidence processes and hence more pronounced sintering effects in the substrate structure. For that reason, it is necessary to take a look at the subsidence behaviour of the felt materials to estimate a nearly realistic influence on the decrease of the substrate porosity that is attributed to the densification processes during cell operation. Figure 4 shows the porosities of felt structure substrates and a standard Crofer22APU knit fabric substrate compared with the substrate thickness that results from simulated subsidence processes.

![Figure 4. Porosity of felt materials and standard Crofer22APU knit fabric substrate compared with total thickness.](image)

Compared with the knit fabric Crofer22APU structure the felt structures show a relatively high porosity. The top layer of the knit fabric structure, that is mainly responsible for the gas distribution and the gas diffusion resistance during cell operation, possesses a thickness of 200 μm and a porosity of merely 33.9 vol%. Together with its basic layer the knit fabric exhibits an overall thickness of approximately 800 μm. In contrast, both nickel felt and FeCrAlY felt show a relatively high porosity. Furthermore, it is remarkable that a simulated subsidence of the FeCrAlY felt structure from a thickness of 1112 μm to 743 μm caused a decrease in porosity from 79.8 vol% to 67.3 vol%. Nearly the same behaviour can be observed in the case of the nickel felt structure. The porosity decreased from 75.4 vol% to 67.0 vol% after a subsidence from 896 μm to 634 μm. This
means that the porosity of both felt materials shows a low dependence on the felt thickness and hence from the subsidence characteristic.

An adequate method to characterise the thermo mechanical behaviour of substrate supported cells is to investigate their principal mechanical adjustment to the MEAs by means of leak rate measurement technique. For this purpose substrate supported half cells were fabricated with anodes consisting of Ni/8YSZ and electrolytes consisting of 8YSZ using typical plasma spray standard parameters from DLR. The cell area was 12 cm$^2$. Figure 5 shows some measured leak rates of half cells on different porous metallic substrates.

According to the real pressure drop on the substrate supported cells during operating conditions, the leak rates in these measurements generally are appointed at 900 mbar. That means that a realistic pressure drop of approximately 100 mbar on the electrolyte layer exists. Hence, in Fig. 5 the nickel felt supported half cell shows the highest electrolyte tightness of all half cells. Its leak rate is $2.9 \times 10^{-4}$ mbar l/cm$^2$ s at 900 mbar and thus nearly one order of magnitude lower than the leak rates of Crofer22APU, FeCrAlY and Plansee ITM 14 half cells.

Although the thermal expansion coefficient (TEC) of nickel is relatively high ($\alpha_{th} = 16-17 \times 10^{-6}$ K$^{-1}$, 30-1000°C) compared with the ferritic steel matrix of the other substrates ($\alpha_{th} = 11-14 \times 10^{-6}$ K$^{-1}$, 30-1000°C), it is possible to fabricate very thin and dense electrolyte layers by plasma spraying. This can be explained by the inherent flexibility of the nickel felt structure that enables it to compensate a strong TEC mismatch between the substrate and the MEA both during plasma spraying and cell operation. Problems with the TEC of the nickel felt structure may only arise with large cell areas (10 x 10 cm$^2$ or 20 x 20 cm$^2$) (7). Generally, this is the reason why in APU stack applications the use of nickel felts is not favoured.
Electrochemical Performance

The porous metallic substrate plays a decisive role in the electrochemical performance of plasma sprayed cells. Oxidation processes of the metallic alloys as well as the substrate properties like the gas permeability, the electrical conductivity, the thermal expansion behaviour and the gas tightness of the electrolyte are dependent on the substrate structure and affect directly the cell performance. For a better understanding of these coherences, I-V characteristic and impedance measurements with cells on different metallic substrate structures were performed. Fig. 6 shows a comparison of the I-V characteristics of different substrate supported cells. The MEA on each substrate consisted of a Ni/8YSZ anode, 8YSZ electrolyte and a LaSrMnO₃ cathode. The cathode was screen printed and the active cell area was 12.54 cm². The cells were measured in simulated reformate gas H₂/N₂ and air at 800°C.

The OCV of the nickel felt cell shows 1085 mV, whereas the OCV of the Crofer22APU cell shows 1040 mV. The OCVs of the FeCrAlY and the Plansee ITM 14 cells are in between. The power density of the nickel felt cell is 211 mW/cm² and significantly higher than the power densities of the other substrate supported cells. According to the leak rate measurements (Fig. 5), the electrolyte density is reflected in the measured OCVs and hence in the power densities.

Another reason for the better performance of the nickel felt cell is the basically higher electrochemical activity of nickel compared with ferritic steel materials. Moreover, the nickel material doesn’t form oxide scales during cell operation as long as hydrogen in the fuel gas is present.
As already mentioned, the nickel felt possesses basically an adequate fibre structure that may compensate a TEC mismatch between the MEA and the felt itself, thus relatively dense electrolyte structures can be fabricated. In contrast, a strong disadvantage of the nickel felt is the post sintering effect during long term operating conditions. Fig. 7 shows SEM images of nickel felt supported cells before and after 900 h cell operation time. The felt structure after the long term operation (Fig. 7b) is significantly compressed by a post sintering effect resulting in significant cell degradation.

Figure 7. SEM images of nickel felt supported cells; a) before cell operation and b) after 900 h cell operation.
CONCLUSIONS

The present paper has given an overview about the different porous metallic substrates used for the vacuum plasma sprayed DLR SOFC concept and some of the investigation methods that were used. Starting from the stack operation requirements, systematic investigations and tests at DLR concerning the structural and material substrate characteristics have been carried out and presented; these include specific electrical conductivity measurements in the model anode gas atmosphere Ar-5% H₂-3% H₂O, porosity investigations by means of quantitative image analysis measurement technique (QIA), leak tests on different substrate supported half cells and finally some electrochemical characterisations of circular cells on different substrates. Basically, it is shown that the electrochemical performance of such substrate supported cells depends strongly on the material and structural characteristics of the metallic substrates.

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