FUNCTIONAL LAYERS FOR THE BIPOLAR PLATES OF PLANAR SOLID OXIDE FUEL CELLS PRODUCED BY VACUUM PLASMA SPRAYING

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ABSTRACT

In the planar Siemens design of the solid oxide fuel cell a metallic bipolar plate is used to separate the single cells. A disadvantage of this chromium based bipolar plate is the formation of highly volatile Cr oxides at the surface of the cathode side leading to a rapid cell degradation. The deposition of a dense perovskite-type oxide layer by vacuum plasma spraying (VPS) avoids the evaporation of chromium oxides. The development of the production process for the deposition of these perovskite-type layers will be described.

INTRODUCTION

The planar design of the Siemens solid oxide fuel cell (SOFC) combining metallic and ceramic materials promises higher current densities and thus smaller dimensions compared to the tubular SOFCs. Furthermore this design has the potential to reduce manufacturing costs and material limitations (1). This planar design consists of several single cell modules which are electrically connected in parallel and in series by bipolar plates directing the process gases to the electrochemically active elements. The principle design of a stack is shown in Fig. 1.

The interconnector material (2) used in the Siemens SOFC design is a chromium based alloy(CrFe5Y2O3). The use of this chromium alloy guarantees a good electrical conductivity, high mechanical stability and a good heat distribution. The thermal expansion coefficient of the chromium alloy is adapted to the coefficient of the electrochemically active elements in order to avoid thermal interface stresses and cracks. This bipolar plate material forms a stable passive layer of Cr2O3 inhibiting a further oxidation of the metal (3). At temperatures above 800°C the Cr2O3 layer forms volatile chromium oxides or chromium hydroxides depending on the oxygen partial pressure (4).
\begin{align*}
\text{Cr}_2\text{O}_3 \text{(s)} + \frac{3}{2} \text{O}_2 \text{(g)} & \Rightarrow 2 \text{CrO}_3 \text{(g)} \tag{1} \\
\text{Cr}_2\text{O}_3 \text{(s)} + 2 \text{H}_2\text{O} \text{(g)} + \frac{3}{2} \text{O}_2 \text{(g)} & \Rightarrow 2 \text{CrO}_2\text{(OH)}_2 \text{(g)} \tag{2}
\end{align*}

The reaction products evaporate and are reduced at the cathode/electrolyte interface to form new crystalline phases (chromium manganese spinels). This process gives rise to strong cell degradation (5). Protective coatings might be successful in preventing the chromium oxide evaporation. The required properties of the protective layers are:

I. high electrical conductivity  
II. a thermal expansion coefficient adapted to the bipolar plate  
III. chemical compatibility to the bipolar plate and the cathode material  
IV. chemical stability up to 1000°C under oxygen atmosphere

Several compositions of perovskite-type oxides fulfil these requirements. Different methods have been tested for the production of protective coatings such as RF-magnetron sputtering, electroplating and chemical vapour deposition. With these methods reliable, dense and adhesive layers could not be deposited (6). The vacuum plasma spraying (VPS) technique has a high potential for the deposition of perovskite layers onto bipolar plates. The application of special torch nozzles (Laval-like nozzles) reduces the particle's residence time in the plasma jet, thus allowing thermally instable materials to be sprayed. The high velocity and laminarity of the plasma jet enables the production of very dense and well-bonded layers. The adaptation of the VPS process and the development of plasma spray parameters for the deposition of protective coatings onto bipolar plates will be presented and the evaluation of such coatings under operating conditions will be discussed.

\section*{MATERIALS AND EXPERIMENTS}

Agglomerated and specially adapted plasma spray powders were used for the deposition of differently doped LaCrO$_3$ and LaMnO$_3$ layers. Fig. 2 shows SEM pictures of these powders. The grain sizes are in the range of -5 + 0.5 µm and the agglomerates are between -60 + 10 µm. According to X-ray diffraction all applied powders are single phase perovskite materials (Fig. 3). Planar CrFe$_5$ parts as well as plates with gas channels were used as substrates. The substrates were sand-blasted in order to roughen the surfaces and to remove the oxide layers. In a further step of development the substrates were activated with a 32% hydrochloric acid.

The bipolar plates were fixed in a vacuum chamber containing a robot handled plasma torch which enables spraying under different angles. For the spray experiments
modified high velocity DLR torches which are based on a PTF4 torch (Sulzer Metco) were used. Main features of these torches are anode nozzles with Laval-like contours and integrated powder injection ports at different locations. For the coating of bipolar plates with the dimension 260 mm x 260 mm a heating device was developed.

Table I summarizes the plasma spray parameters used for the processing of the perovskite powders.

Table I: Used plasma spray parameters

| Torch power | Plasma gas feed rate | Chamber pressure | Spray distance |
|-------------|----------------------|------------------|----------------|
| 16-35 kW    | 40-55 SLpM Ar        | 80-150 mbar      | 120-240 mm     |

Phase stability and crystallinity of the layers were checked by X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX). The microstructure and porosity of the layers were investigated by optical and scanning electron microscopy. Overall coated samples were annealed under operating conditions in contact to a cathode at 950°C for 1000 h. Additionally, chromium oxide evaporation was measured in order to prove the protective property of the layers (6).

RESULTS AND DISCUSSION

Plasma Spray Parameter Optimization

The plasma spray parameter variation was performed in order to determine the conditions for obtaining dense, well bonded chromite and manganite layers on bipolar plate material without decomposition of the perovskite phase. Thus, the powder has to be injected at a nozzle position where the plasma temperature is adjusted to melt the perovskite particles without decomposition. The residence time of the particles in the plasma jet should be as short as possible. Dense layers can be obtained if the plasma jet and the powder particles possess high kinetic energy at their impact on the substrate surface. The fulfilment of these requirements is a special task for the high velocity nozzles designed at the DLR.

For the use of perovskite-type layers as protective coatings for bipolar plates the surface roughness should be below 5 µm. The sand-blasting pretreatment of the substrate surface causes a roughness of up to 10 µm and can therefore not be applied. Other reasons to avoid sand-blasting are the formation of mechanical stresses in the bipolar plate and the damage of the gas channel contours by this method. An alternative pretreatment was developed by means of etching the interconnector material with
32 % HCl solution. A comparison of the two different pretreatment methods is shown in Fig. 4. The sand-blasting was therefore no longer applied and replaced by etching.

The results of the plasma spray parameter optimization were shown in Fig. 5 and Fig. 6. High crystallinity and single phase perovskite were found when using the optimized set of parameters (Fig. 5). The cross-section of an optimized layer is shown in Fig. 6. The layer is almost dense with a good adhesion to the CrFe5 plate.

**Plasma Spraying onto Structured Bipolar Plates**

The next step of the investigation was the development of a plasma spray process for the deposition of the materials onto structured bipolar plates. Fig. 7 shows a typical result of the deposition onto bipolar plates with gas channels which have vertical flanks. Almost no deposition is observed on the flanks. A change of the gas channel contour and a variation of the spray angle during the deposition led to sufficiently overall dense and adhesive protective layers (Fig. 8).

A further step was the scale up of the deposition process to produce layers for bipolar plates with the dimension 260 mm x 260 mm. During the coating process of these large plates a thermal gradient occurs which leads to thermal stresses. These stresses induce cracks or bulges, finally resulting in destroyed bipolar plates.

To avoid high thermal stresses, a preheating device was installed for the CrFe5 plates. Prior to the coating process the plates were heated up to 500°C. The thermal gradients are reduced enormously during deposition and the interconnector plate has now a much more ductile behaviour. When applying the heating device cracks did no longer appear and thus the protective layer could also be deposited onto the large plates without deformation or destruction.

**EVALUATION OF PROTECTIVE LAYERS**

The protective function of the plasma sprayed layers was demonstrated by means of chromium evaporation measurements. The detected chromium content of the investigated bipolar plates coated with a doped LaMnO3 layer was in the range of detection accuracy. After annealing no reaction products of evaporated chromium oxides could be detected on cathodes in intimate contact with the coated bipolar plates.

In single cell housings coated CrFe5 plates were applied as electrical contacts on the cathode side whereas a Pt grid was used on the anode side. The MEA (membrane-electrode-assembly) consisted of a 150 mm YSZ electrolyte membrane with a 50 µm La1-xSrₓMnO3 cathode layer and a 50 µm NiO-YSZ anode layer. The electrode area was
16 cm². Cell measurements were performed under galvanostatic conditions at 950°C in oxygen and dry hydrogen. Previous experiments using non-coated interconnector plates resulted in fast cell degradation caused by a deposition of chromium oxide compounds in the cathode (7). Cells with Sr and Ca doped LaCrO₃ or LaMnO₃ coated interconnectors were stable during 1000 hours of operation (Fig. 9).

CONCLUSION

The utilization of high velocity nozzles designed by the DLR and a careful adaptation of the spray parameters succeeded in the production of dense perovskite-type chromite and manganite layers on bipolar plates by vacuum plasma spraying. Improved treatment of the substrate surface leads to a very good adhesion between layer and substrate. The deposition onto structured bipolar plates was a challenge which could successfully be addressed by developing a deposition process using a spray robot and by changing the gas channel geometry. Thermal gradients in the bipolar plate during the coating process were minimized by using a heating device. The feasibility of the reproducible production of protective coatings on 260 mm x 260 mm plates was proved.

The protection of the bipolar plate against chromium oxide evaporation by means of VPS coatings was proved by evaporation tests and annealing tests under operating conditions. Up to now the VPS technique represents the best method for producing reliable protective layers for the bipolar plate.

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Fig. 1: Principle design of a stack

Fig. 2: SEM pictures of agglomerated Sr doped LaCrO₃ powder
Fig. 3: X-ray diffraction pattern of the Sr doped LaCrO$_3$ powder

Fig. 4: SEM pictures of pre-treated substrates, a: sand-blasted, b: etched
Fig. 5: X-ray diffraction pattern of plasma sprayed Sr doped LaCrO$_3$ layers

Fig. 6: SEM picture of an optimized (La, Sr)CrO$_3$ coating
Fig. 7: Bipolar plate with vertical gas channels coated with a perovskite layer

Fig. 8: Bipolar plate with the current gas channel design coated with a chromite layer
Fig. 9: Cell measurement at 950°C using $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ coated interconnector plates