

# High-Velocity DC-VPS for Diffusion and Protecting Barrier Layers in Solid Oxide Fuel Cells (SOFCs)

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High-temperature fuel cells of the solid oxide fuel cell (SOFC) type as direct converter of chemical into electrical energy show a high potential for reducing considerably the specific energy consumption in different application fields. Of particular interest are advanced lightweight planar cells for electricity supply units in cars and other mobile systems. Such cells, in one new design, consist mainly of metallic parts, for example, of ferrite steels. These cells shall operate in the temperature range of 700 to 800 °C where oxidation and diffusion processes can be of detrimental effect on cell performance for long-term operation. Problems arise in particular by diffusion of chromium species from the interconnect or the cell containment into the electrolyte/cathode interface forming insulating phases and by the mutual diffusion of substrate and anode material, for example, iron and chromium from the ferrite into the anode and nickel from the anode into the ferrite, which in both cases reduces performance and system lifetime. Additional intermediate layers of perovskite-type material, (e.g., doped  $\text{LaCrO}_3$ ) applied with high-velocity direct-current vacuum plasma spraying (DC-VPS) can reduce such effects considerably if they are stable and of high electronic conductivity.

**Keywords** diffusion barrier layers high-velocity DC-VPS, perovskite type  $\text{LaCrO}_3$ , solid oxide fuel cell

## 1. Introduction

At present, the electrical power in cars is usually provided by a generator connected to the crankshaft of the internal combustion engine (ICE). Initially, the main task of this generator was to supply electricity for the headlights and to charge the battery (Ref 1). In the meantime the power demand of cars has increased considerably, and this demand is still rising. The direct link between the generator and the ICE means at least at part-load operation of the engine, low efficiency of the system, and economic limits for increasing the generator and the number of parts needing electricity. Also, it requires an operation of the engine even at idling of the car to get electricity, for example, for air conditioning. Therefore, there exists a high activity worldwide to develop ICE-independent generators, so-called auxiliary power units (APU), which preferably can be operated with on-board fuels.

Recent improvements in fuel cell technology have increased the attractiveness of these energy converters with their potential for very high efficiency values. Of the different fuel cell types,

solid oxide fuel cells (SOFC) in particular are favored for APUs because the effort for reforming and cleaning of gasoline, diesel, or other hydrocarbons to get a suitable fuel is relatively low. Also, in contrast to low-temperature fuel cells with polymer membranes (PEM) and platinum catalysts, carbon monoxide (CO) represents a usable fuel component. To the main requirements for a broad use of SOFCs as APUs in cars belong particularly reliability, sufficient operating time, high power density at low weight and volume, a high tolerance for fast heating up and thermal cycling, and attractive costs for production, where for the latter demand plasma spraying offers a great potential.

## 2. Principle, Function, and Materials of SOFCs

To understand the present development tasks and the importance of the presented work, the principle of a (planar) SOFC has to be described by Fig. 1. It usually consists of an electrolyte of zirconia doped with yttria (YSZ) or scandia (ScSZ) for stabilization of the high-temperature cubic zirconia phase and to increase the electrical conductivity for oxygen ions, which—not the electrons—are the charge carriers in SOFCs. This gastight component is covered on both sides with the two porous electrodes, namely cathode and anode. The oxygen ions are generated on the cathode side by dissociation of the oxygen molecules in the airflow and the reduction of each of the resulting atoms by adding two electrons. The negatively charged oxygen ions then migrate through the electrolyte due to a concentration gradient toward the electrolyte/anode interface. At the electrolyte/anode interface, the incoming fuel gas components of hydrogen (and/or CO) react with the oxygen ions where electrons are released to return to the cathode via an external load. Both electrodes are mixed-conducting materials, that is, conducting for oxygen ions

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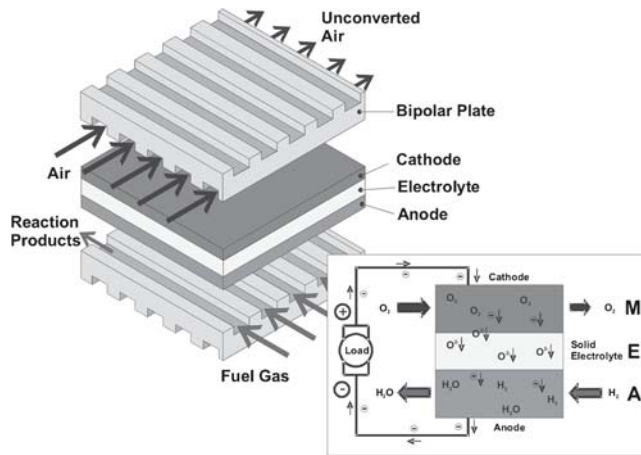


Fig. 1 Design and principle of a planar SOFC

and electrons. They consist, at the cathode side, of a perovskite-type material such as lanthanum strontium manganite (LSM) and at the anode side usually of a Ni/8YSZ cermet.

At operating conditions, a voltage between 0.5 and 1 V is generated by each cell at a current density of up to about 1 A/cm<sup>2</sup>. To get a technically usable voltage and power level several cells have to be combined to a stack, in which so-called bipolar plates or interconnects are used to provide the electrical connection between the cells. These interconnects are also used to separate and supply the reacting gases and to take care of the disposal of the reaction products. Current SOFCs for stationary application operate somewhere in the temperature range of 800 to 1000 °C. Their mechanical stability is either provided by a relatively thick electrolyte or by a robust supporting anode. In the latter design, the electrolyte can be very thin resulting in reduced internal losses and improved performance. Conventionally, such cells are made by wet powder processing and sintering technology (Ref 2). As described previously, to the main requirements using SOFCs as APUs in cars belong sufficient operating time, a high tolerance for fast heating up and thermal cycling, and also low production costs. Therefore, means have to be developed to bring down the operating temperature. Also the cell design has to be modified to allow for the required thermal properties and for inexpensive production.

### 3. Plasma Spray Approach for a New Type of Planar SOFCs—Description of Development Tasks

For several years, the German Aerospace Research Center (DLR, Stuttgart, Germany) has been active in this field with its own plasma spray concept, where the cell layers are plasma sprayed in a vacuum chamber at reduced atmosphere with specifically optimized parameters using DLR high-velocity plasma torches with Laval supersonic nozzles (Fig. 2) where mostly the M3-type is applied by DLR for the considered purposes (Ref 3, 4). In comparison to the well-established sintering techniques, plasma spray methods have the advantage that the final quality of plasma deposited cells is obtained immediately with deposi-

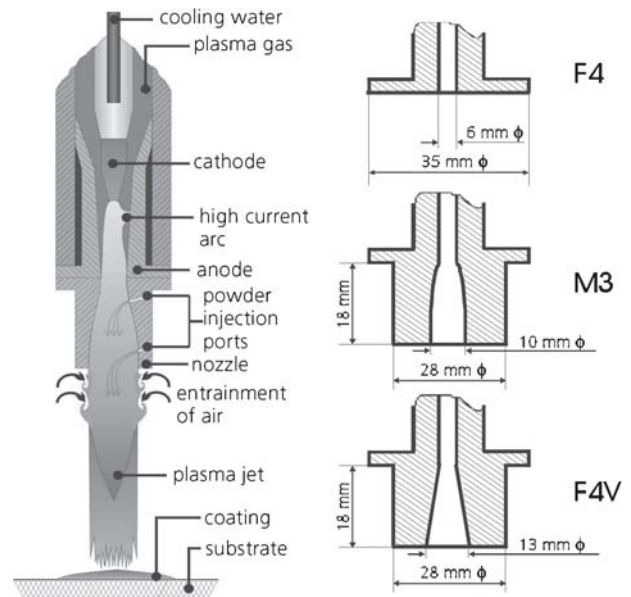


Fig. 2 Principle of a direct current plasma torch with Laval nozzle M3

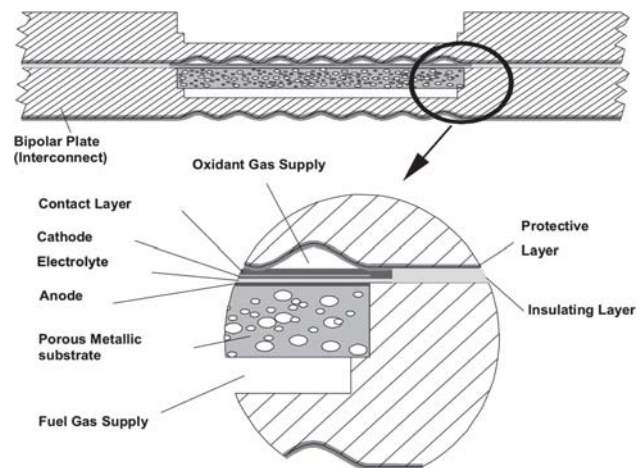
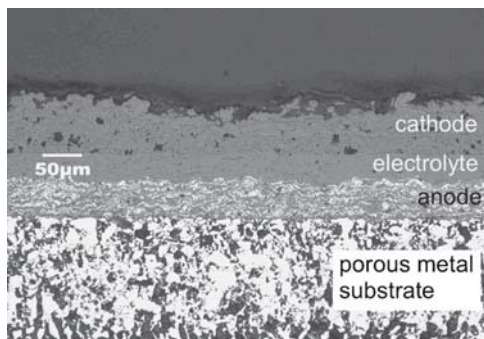


Fig. 3 Principle of the DLR-SOFC plasma spray concept

tion, in most cases not needing time-consuming postthermal processing as with conventional sintering techniques requiring high sintering temperatures.

The DLR cells are deposited on porous metallic substrates (Fig. 3) that also serve as fuel gas distributors on the anode side. In this case, the whole electrochemically active and thermally sensitive ceramic part of the cell can be as thin as about 100 μm. To match the coefficient of thermal expansion of the electrolyte (approx.  $11 \times 10^{-6} \text{ K}^{-1}$ ) and to reduce material costs, the porous metallic substrates are also made of a ferrite-type material similar to the interconnect (Ref 5). Figure 4 shows a cross section of such a plasma sprayed cell. On the cathode side the cells “see” the metallic chromium-containing interconnect, on the anode side the porous substrate is fixed to the next interconnect for electrical series connection. With such cells, power densities of about 300 mW/cm<sup>2</sup> at 800 °C with simulated reformed gasoline



**Fig. 4** Plasma sprayed SOFC on porous ferrite substrate (cross section) consisting of a Ni/8YSZ-anode, a 8YSZ-electrolyte, and a LSM cathode

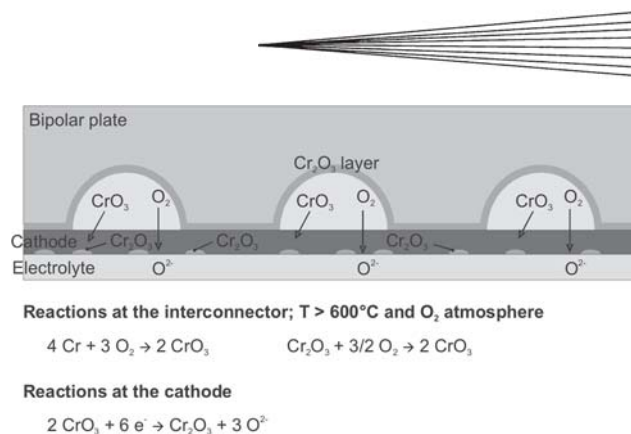
can be obtained, at present (Ref 6). However, as the authors' investigations revealed, very short operating hours can be sufficient to show severe degradation and destabilizing effects occurring due to the formation of unfavorable phases at the cathode/electrolyte and the anode/substrate interfaces. The cause of the degradation and destabilization for the cathode side is chromium (Cr) species diffusion from the interconnect, and for the anode/substrate interface it is caused by the mutual diffusion of nickel (Ni) and iron (Fe) and Cr.

Several papers appeared recently that describe how plasma spraying was applied to make components and even all three layers of cells. For instance in Ref 7, the properties of a triple torch reactor are studied to make the three layers consisting of a graded cermet anode, a YSZ electrolyte, and a perovskite cathode. Following to Ref 8, air plasma spraying was used to develop these three layers for intermediate temperature SOFCs. However, with exception of Ref 9 of 1999, where for an open-cell system the development of protection coatings for metallic-substrate supported SOFCs is described using atmospheric plasma spraying (APS), this topic was only recently touched on due to the progress with technical cells and the deeper experience with problems arising with practical operation. For example, a more recent publication (Ref 10) can be cited with interconnect coatings consisting of lanthanum strontium manganite (LSM) applied by APS. In this situation, DLR came back to its experience with lanthanum strontium chromite (LSCR), applied with DC-VPS to get immediately dense coatings for chrome-based interconnect alloys. This was in accordance with the goal to produce the whole cell by plasma spraying. Therefore, the interdiffusion problem, a solid-body effect between the Ni of the anode and Fe and Cr of the substrate, was also approached with adapted VPS process.

## 4. HV-VPS Coating against Cr Release from the Interconnect

### 4.1 Description of the Phenomenon Defining the Task

Chromium-base alloys as well as chromium-containing steels are preferred as interconnect materials in advanced planar SOFC designs. Such alloys as the oxide-dispersive strengthened



**Fig. 5** Chromium diffusion at Cr-containing ferrite interconnect and on cathode/electrolyte interface

(ODS) alloy of Cr-5Fe-1Y<sub>2</sub>O<sub>3</sub> (Ref 11) and the specifically developed steel of CroFer 22 APU (Ref 12) are protected from corrosion by a chromium scale (Cr<sub>2</sub>O<sub>3</sub>) formed in the oxidizing atmosphere of the cathode side, as shown principally in Fig. 5.

At the cathode side under SOFC operating conditions (about 800 °C) where a considerable water (steam) partial pressure of about 0.02 bar exists beside oxygen, volatile chromium (VI) species (CrO<sub>3</sub>, CrO<sub>2</sub>(OH)<sub>2</sub>, and CrO<sub>2</sub>OH) are formed in the Cr<sub>2</sub>O<sub>3</sub> layer material of the interconnect (Ref 13). These volatile species can be reduced to solid chromium (III) oxides at the critical electrochemically active triple-phase boundary between the cathode and electrolyte resulting in a severe degradation of cell performance (Ref 13, 14).

### 4.2 Approach for Solving the Cr Release Problem

There are two potential principal methods to reduce the chromium evaporation:

- Reduction of the operating temperature, which is a limited option
- Application of a ceramic protective coating for chromium retention

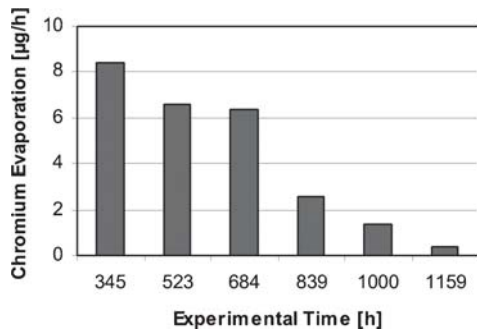
For the latter method, acceptor-doped perovskites were chosen to make dense coatings of about 30 μm thick with DC-VPS. Main requirements to be fulfilled by the coating material are:

- Chemical compatibility to the cathode and interconnect
- Chemical stability in the cathode atmosphere at temperatures up to 1000 °C
- High electrical conductivity (>10<sup>2</sup> S m<sup>-1</sup> at 800 °C)
- Coefficient of thermal expansion (CTE) similar to that of the interconnect material

Corresponding to these requirements, three different candidates for protective layers were chosen for the spray experiments on ferrite samples. The specifications of these powders are shown in Table 1.

The chromium vaporization rates of the samples were measured and compared with the values obtained for the uncoated ferrite samples under the same experimental conditions (Ref 13, 14). Best results were obtained by La<sub>0.9</sub>Sr<sub>0.1</sub>CrO<sub>3</sub>. It is interesting that the Cr retention effect is dependent on operating time as





**Fig. 6** Time effect on Cr species evaporation (in the case of  $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$ )

**Table 1** Specification of used plasma spray powders for Cr evaporation preventing layers

Composition	Particle size	Supplier
$\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$	$-32 + 16 \mu\text{m}$	EMPA, Switzerland
$\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$	$-32 + 16 \mu\text{m}$	Medicoat, Switzerland
$\text{La}_{0.99}\text{Cr}_{0.72}\text{Mg}_{0.16}\text{Al}_{0.12}\text{O}_3$	$-32 + 16 \mu\text{m}$	DLR, Germany

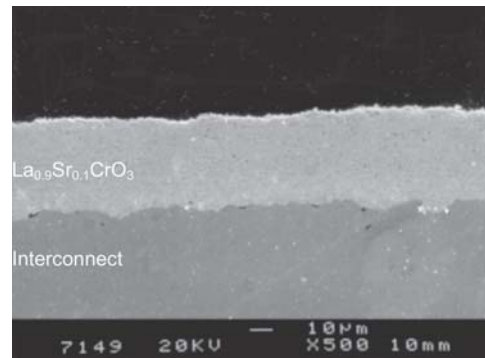
shown in Fig. 6, where after 1000 h Cr evaporation is almost negligible. Figure 7 shows a scanning electron micrograph of the cross section of the DC-VPS perovskite coatings indicative of very high coating quality. Optimum spray parameters were achieved by using  $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$  with a grain size fraction of  $-32 + 16 \mu\text{m}$ .

## 5. DC-VPS Diffusion Barrier Layer between Anode and Substrate

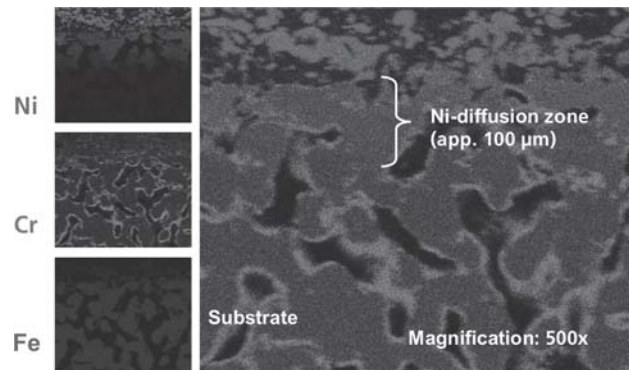
### 5.1 Description of the Phenomenon Defining the Task

As previously mentioned, SOFCs for automotive APUs should exhibit short start-up times. Therefore, advanced designs mostly consisting of metal of high thermal conductivity with very thin cells can have the potential to meet this requirement. In this respect, DLR is active with its own approach with porous metallic substrates at the anode side representing the base on that anode; electrolyte and cathode are consecutively plasma sprayed in thin layers. These substrates have to be fixed to the anode side of the interconnect and consist also preferably of ferrite materials with a fairly high chromium and manganese content (Ref 15). Such materials show good corrosion stability, and their CTE is close to that of the critical electrolyte. However, at high operating temperatures atomic transport processes during long operating times can cause destructive structural alterations. In particular, the substrate/anode interface represents a problem area. For example, solid-state diffusion of Fe, Cr, and Ni between the Ni/YSZ anode and the ferrite steel based substrate can take place as seen in Fig. 8.

One of the apparent problems is the transformation of the ferrite into the austenitic phase due to Ni diffusion resulting in a considerable increase of the CTE.



**Fig. 7** Scanning electron micrograph (SEM) of a protective perovskite coating on interconnect (Detector: Topcon DS 130)



**Fig. 8** EDX map of a Ni/8YSZ anode on a sintered porous ferrite substrate after 550 h at 800 °C in Ar-5% $\text{H}_2$ -2% $\text{H}_2\text{O}$  atmosphere

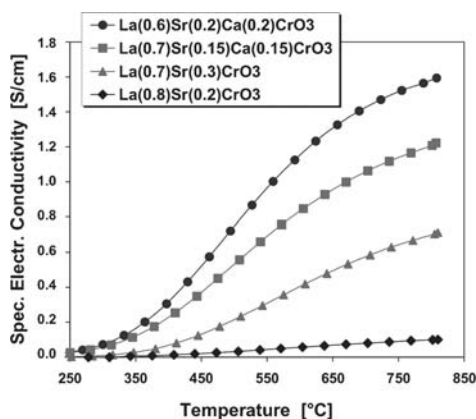
### 5.2 Approach for Solving the Interdiffusion Problem

To prevent the described diffusion and other negative effects, the solution was to apply a diffusion barrier layer that should exhibit the following properties:

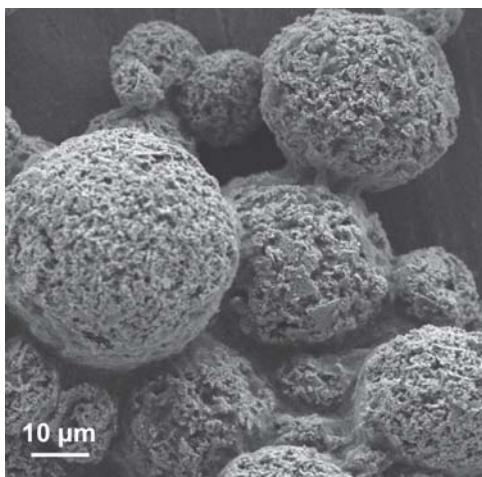
- Coating of the solid parts of the substrate without closing the pores
- Matching the CTEs of substrate and anode
- High electronic conductivity in reducing atmospheres
- Chemical stability in reducing and humid anode atmospheres and low swelling behavior
- Barrier effect for Fe, Cr, and Ni species
- Electrochemical compatibility to the other cell components at operating conditions (inert in chemical respects)

Due to the promising experience with the interconnect coatings, the material choice was also directed to the perovskite-type materials (Table 2), in particular to differently doped  $\text{LaCrO}_3$  perovskites (Ref 16). Based on results of literature study of CTE values, the temperature dependence of the specific electrical conductivity of some candidate perovskite materials for the diffusion barrier was measured. Some representative curves are shown in Fig. 9.

This study was followed by vacuum plasma spray experi-



**Fig. 9** Temperature dependence of the specific electrical conductivity of differently doped  $\text{LaCrO}_3$  perovskites measured in  $\text{Ar-5\%H}_2$  atmosphere

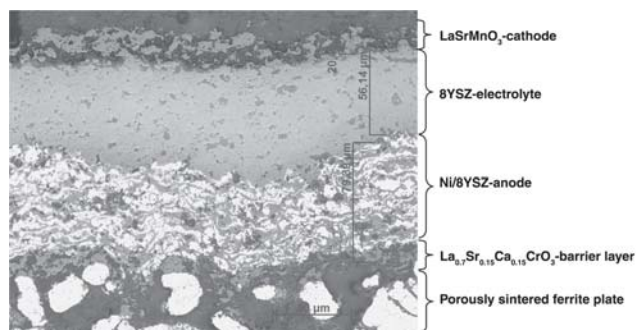


**Fig. 10** Scanning electron micrograph (SEM) of a typical  $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$  powder ( $-32 + 16 \mu\text{m}$ ) for plasma spraying of the diffusion barrier on the anode side. Detector: Topcon DS 130

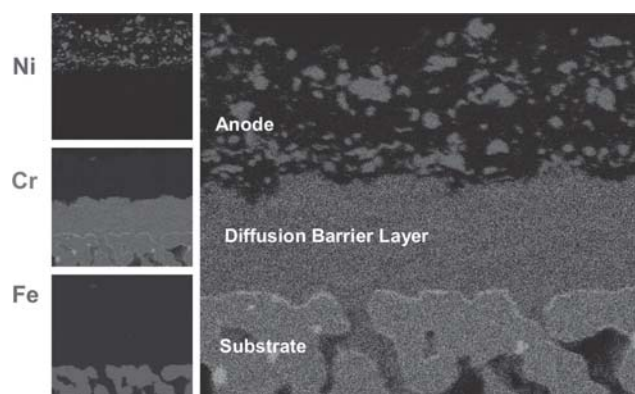
**Table 2** Specification of doped  $\text{LaCrO}_{30}$  compositions for diffusion barrier layers at substrate/anode interface

Composition	Particle size	Supplier
$\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$	$-32 + 16 \mu\text{m}$	EMPA, Switzerland
$\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$	$-32 + 16 \mu\text{m}$	Medicoat, Switzerland
$\text{La}_{0.6}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{CrO}_3$	$-32 + 16 \mu\text{m}$	HC Starck, Germany
$\text{La}_{0.7}\text{Sr}_{0.15}\text{Ca}_{0.15}\text{CrO}_3$	$-32 + 16 \mu\text{m}$	HC Starck, Germany

ments with agglomerated powders; an example is shown in Fig. 10. These experiments are still not fully finished. However, the results are nevertheless encouraging, as demonstrated by Fig. 11 with the cross section of a  $\text{LaSrCrO}_3$  perovskite interlayer between a Ni/8YSZ anode and a porous sintered ferrite substrate after 200 h of cell operating time at  $800^\circ\text{C}$  with  $50\%\text{H}_2/50\%\text{N}_2$  and air. Figure 12 depicts the energy dispersive x-ray (EDX) map showing almost no mutual material diffusion after the test with these simulated operating conditions.



**Fig. 11** Cross section of a plasma sprayed cell with  $\text{LaCrO}_3$  diffusion barrier layer between Ni/8YSZ anode and porous ferrite substrate after 200 h at  $800^\circ\text{C}$



**Fig. 12** EDX map of a Ni/YSZ anode on a ferrite substrate with  $\text{LaCrO}_3$  barrier layer after 200 h at  $800^\circ\text{C}$  in  $\text{Ar-5\%H}_2\text{-2\%H}_2\text{O}$

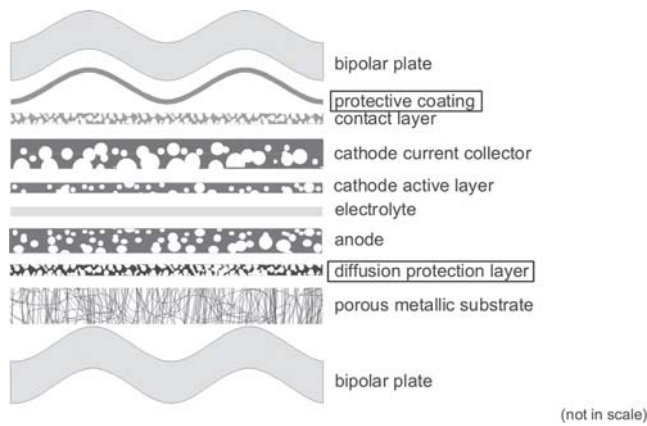
At present, these experiments can be summarized as:

- $\text{LaCrO}_3$  compositions used for diffusion barrier (see also Table 2) were  $\text{La}_{0.7}\text{Sr}_{0.3}\text{O}_3$ ,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ ,  $\text{La}_{0.6}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{CrO}_3$ , and  $\text{La}_{0.7}\text{Sr}_{0.15}\text{Ca}_{0.15}\text{CrO}_3$ .
- The barrier effect for Fe, Cr, and Ni species could be demonstrated with each of these compositions.
- Problems can occur with swelling (removal of oxygen from perovskite matrix combined with a volume expansion) of the qualified perovskite-type  $\text{LaCrO}_3$ .

Therefore, more work is needed to further improve compositions, layer structure, and plasma spray parameters and also to investigate the electrochemical compatibility and long-term behavior.

## 6. Conclusions

As with the production of the three electrochemically active SOFC layers, anode, electrolyte, and cathode, the two additive layers necessary with such “metallic” SOFC designs—that is, the chromium evaporation preventing coating for the ferrite interconnect and the diffusion barrier layer between the anode and the porous ferrite substrate—can be successfully made by DC-VPS with specific powdery precursor materials. In this case, a



**Fig. 13** Schematic of the DLR-SOFC design with the different layers on a metallic substrate

planar SOFC is built up as principally shown in Fig. 13. Both additive layers result in reduced degradation effects and hence in extension of the lifetime of such DLR plasma sprayed cells which, at present development state, deliver about 300 mW/cm<sup>2</sup> at 800 °C with simulated gasoline reformat (H<sub>2</sub>/N<sub>2</sub>) as fuel.

Despite the promising results, further work has to be done to improve the power density, to reduce the degradation effects to extend lifetime, furthermore, to make spraying of the whole cell more efficient by an improved process with higher deposition efficiency, and, in particular, to develop production means and equipment allowing for an efficient, economical, and automated serial production as precondition for a technical breakthrough of the plasma technology application for cells and stacks of APUs and in particular of such APUs.

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