

Diffusion and Protecting Barrier Layers in a Substrate Supported SOFC Concept

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Abstract

High temperature fuel cells of 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 light-weight planar cells for electricity supply systems in cars and other mobile systems. Such cells, in one current design, consist mainly of metallic parts, e.g. 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 volatile Cr-species from interconnects into the triple phase boundary (TPB) on the cathode side forming electrochemical reaction inhibiting phases. Furthermore, on the anode side a mutual diffusion of ferritic substrate and anode material, e.g. iron and chromium from the ferrite into the anode and nickel from the anode into the ferrite can occur resulting in undesirable phase and structure transformations. Both cases of degradation mechanisms significantly reduce performance and system lifetime. A possible solution of these problems is seen in protecting intermediate layers, which can reduce such effects considerably if they are dense, stable and of high electronic conductivity. Perovskite-type layers (e.g. doped LaCrO_3) applied with high-velocity Direct Current-Vacuum Plasma Spraying (DC-VPS) promise to solve reliably such problems.

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 [1]. In the meantime the power demand 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, economic limits for increasing the generator and the number of electricity needing parts. Also, it requires an operation of the engine even at idling of the car to get electricity e.g. for air conditioning. Therefore, there exists a high ac-

tivity world-wide 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 of very high efficiency values. Of the different fuel cell types, Solid Oxide Fuel Cells (SOFCs) in particular are favoured for APUs because the effort for reforming and cleaning of gasoline, diesel or other hydrocarbon gases to get a suitable fuel is relatively low. Also, in contrast to low temperature fuel cells with polymer membranes (PEMs) and platinum catalysts, carbon monoxide (CO) represents a usable fuel component.

Present state SOFCs for stationary application are operated somewhere in the temperature range of 800 to 1000°C. Their mechanical stability is either provided by a relatively thick electrolyte or by a supporting robust anode where with 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 [2]. One of the main requirements using SOFCs as APUs in cars is besides reliability, sufficient operating time, high power density at low weight and volume, and a high tolerance for fast heating-up and thermal cycling. 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. For several years DLR Stuttgart, Germany, is active in this field by developing its own plasma spray concept, where the cell layers are plasma sprayed in a vacuum chamber at reduced atmosphere with specifically adapted parameters applying their high-velocity plasma torches with Laval supersonic nozzles (Fig. 1) [3, 4]. In comparison to the well established sintering techniques plasma methods have the advantage that with the performed spray process the final quality is obtained and no time consuming thermal process is needed afterwards where material and structure alterations can take place at the required high sintering temperatures.

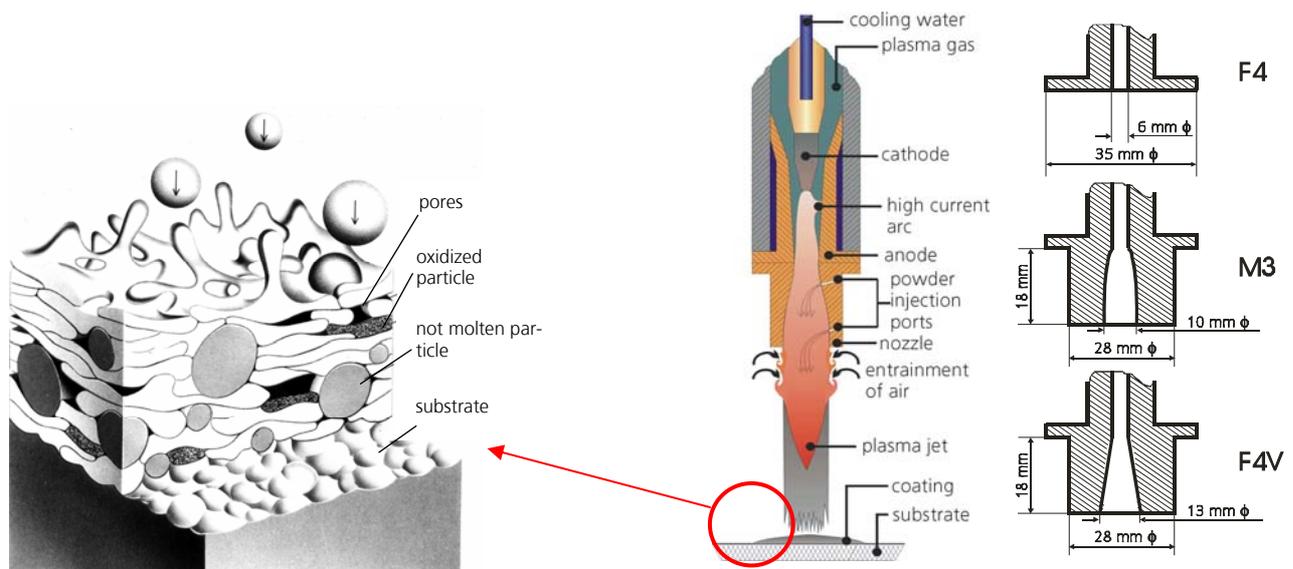


Figure 1. Layer formation on a substrate (left) [5] and principle of a DC-plasma torch with Laval nozzle M3 (right)

The DLR cells are commonly sprayed on a porous metallic substrate as shown in Fig. 1 and 2 which serves also as fuel gas distributor and as mechanical cell support on the anode side.

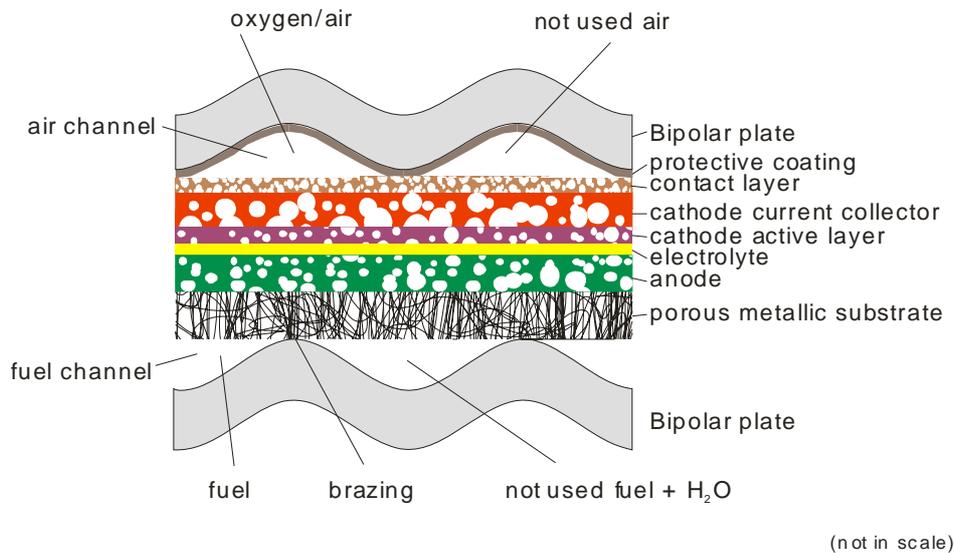


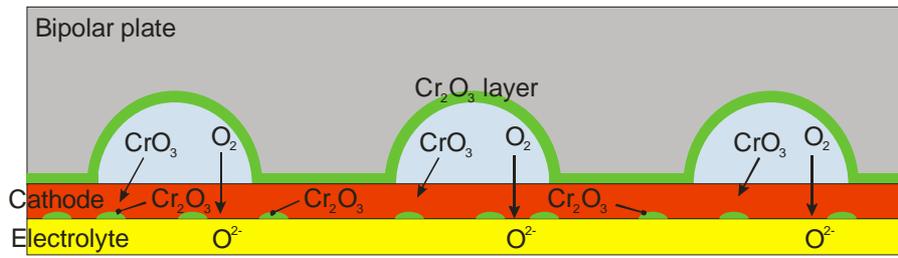
Figure 2. Principle of the planar metal substrate supported SOFC concept of DLR-Stuttgart

In this case the thermal sensitive ceramic part of the cell can be very thin with about 100 μm . To match the coefficient of thermal expansion (CTE) of the electrolyte (approx. $11 \times 10^{-6} \text{ 1/K}$, 30-1000°C) and to reduce material costs the substrate consists of a ferrite type material similar to the interconnect. Concerning this, the DLR has performed for some years developments with different substrate types and partners from industry which are described in detail elsewhere [6, 7].

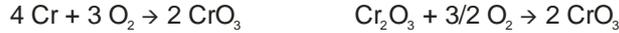
There are two significant degradation processes which can emerge both in this and in other SOFC-concepts. On the one hand, by diffusion of volatile Cr-species from interconnects into the triple phase boundary (TPB) on the cathode side electrochemical reaction inhibiting phases can occur. On the other hand, on the anode side a mutual diffusion of ferritic substrate and anode material, e.g. iron and chromium from the ferrite into the anode and nickel from the anode into the ferrite can result in not wishful phases and structure transformations. Both cases of degradation mechanisms significantly reduce performance and system lifetime. A possible solution of these problems are seen in protecting intermediate layers, which can reduce such effects considerably if they are dense, chemical stable and of high electronic conductivity. Perovskite-type layers (e.g. doped LaCrO_3) applied with high-velocity Direct Current-Vacuum Plasma Spraying (DC-VPS) promise to solve reliably such problems.

DC-VPS Protective Coating against Cr-Release from the Interconnect

Chromium-based alloys as well as chromium-containing steels are preferred as interconnect materials in advanced planar SOFC designs. Such alloys like the ODS (oxide-dispersive strengthened)-alloy of $\text{Cr}_5\text{Fe}_1\text{Y}_2\text{O}_3$ [8] and the specifically developed steel of CroFer 22 APU [9] are protected from corrosion by a chromium scale (Cr_2O_3) formed in the oxidizing atmosphere of the cathode side as shown principally in Fig. 3.



Reactions at the interconnector; $T > 600^\circ\text{C}$ and O_2 atmosphere



Reactions at the cathode

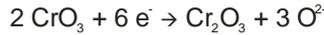


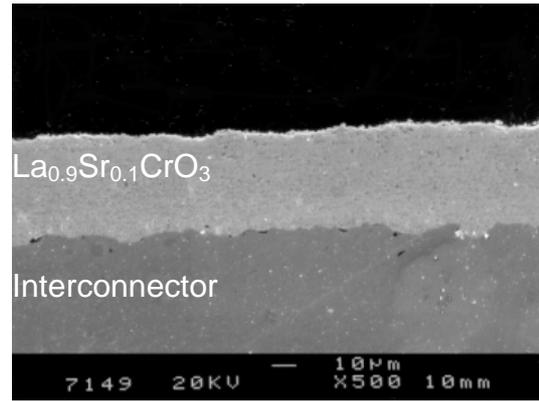
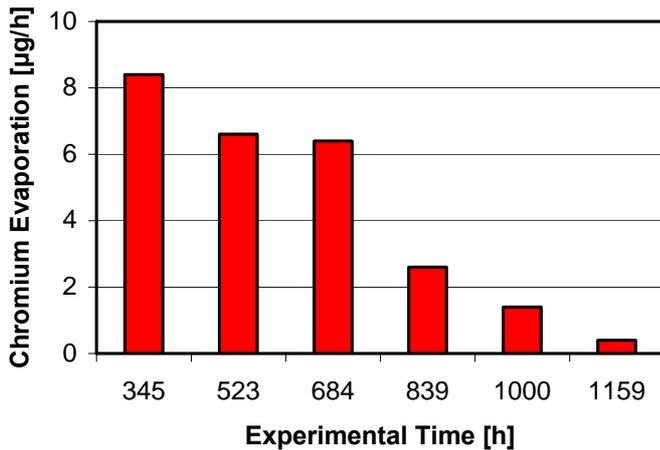
Figure 3. Chromium diffusion at Cr-containing ferrite interconnect and on cathode / electrolyte interface

At the cathode 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_3 , $\text{CrO}_2(\text{OH})_2$ and CrO_2OH) can be formed in the Cr_2O_3 layer material of the interconnect [10]. 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 [11]. There are two potential methods to reduce the chromium evaporation: reduction of the operating temperature, which is a limited option, and application of a ceramic protective coating for chromium retention. For the latter method, acceptor doped perovskites were chosen to make $30 \mu\text{m}$ thick dense coatings with high velocity vacuum plasma spraying. 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 ($> 1 \text{ S cm}^{-1}$ at 800°C) and a coefficient of thermal expansion (CTE) similar to the interconnect material. Corresponding to these requirements three different candidates for protective layers were chosen for the spray experiments on ferrite samples and the resulting VPS-layers were thoroughly investigated and tested. The specifications of these powders are shown in Tab. 1.

Table 1. Specification of used plasma spray powders protecting interconnect 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

The chromium vaporisation rates of the samples were measured and compared to the values obtained for the uncoated ferrite samples under the same experimental conditions [10]. Best results were obtained by $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$. It is interesting that the Cr-retention effect is depending on operating time as shown in Fig. 4a, where after 1000 hrs Cr-evaporation is almost negligible.



a.

b.

Figure 4. a. Time effect on chromium species evaporation (in the case of $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$)
 b. SEM of a protective perovskite-coating on interconnects

Figure 4b shows an SEM 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 $-32+16\ \mu\text{m}$.

DC-VPS diffusion barrier layer between anode and substrate

As already mentioned above SOFCs for car APUs should exhibit short start-up times. Therefore, an advanced design mostly consisting of metal of high thermal conductivity with very thin cells can have the potential to meet this requirement. With this respect DLR is active with its own approach where porous metallic substrates at the anode side represent the base on which anode; electrolyte and cathode are consecutively plasma sprayed in thin layers. These substrates are preferably ferrite materials with a fairly high chromium and low manganese content [12]. Such materials show good corrosion stability and their coefficient of thermal expansion is close to that of the critical electrolyte. But, at the high operating temperatures atomic transport processes during long operating times can cause destructive structure alterations. In particular, the substrate/anode interface represents a problem area. For example, diffusion of Fe-, Cr- and Ni-species between the Ni/YSZ anode and the ferrite steel based substrate can take place as seen in Fig. 5.

It can be recognized that a significant diffusion process of nickel took place with a diffusion zone of approx. $60\ \mu\text{m}$. Hence, the ferritic steel matrix is altered at least partially into an austenitic structure, in which the CTE is significantly increased in this diffusion area. Thus, a mismatch of CTE between the substrate and the ceramic cell components can occur resulting in crack formation in particular in the electrolyte and hence in a breakdown of the cell within short operating times. In contrast, a diffusion of Fe- and Cr-species from the ferrite substrate matrix into the anode up to the anode/electrolyte interface could also be observed at DLR with some studies [13, 14]. In this case, the iron and chromium species theoretically can migrate in the form of Fe, Fe^{2+} , Fe^{3+} , Cr, and Cr^{3+} and react directly with the oxygen ions coming from the 8YSZ phase to FeO , Fe_2O_3 , CrO_3 and Cr_2O_3 .

These oxide phases could be detected both in the anode itself and in the anode/electrolyte interface within these studies. The cell detrimental effect of this oxide formation can be described by a volume expansion due to oxide phase forming, resulting at the same time in a cracking of the electrolyte with cell operation.

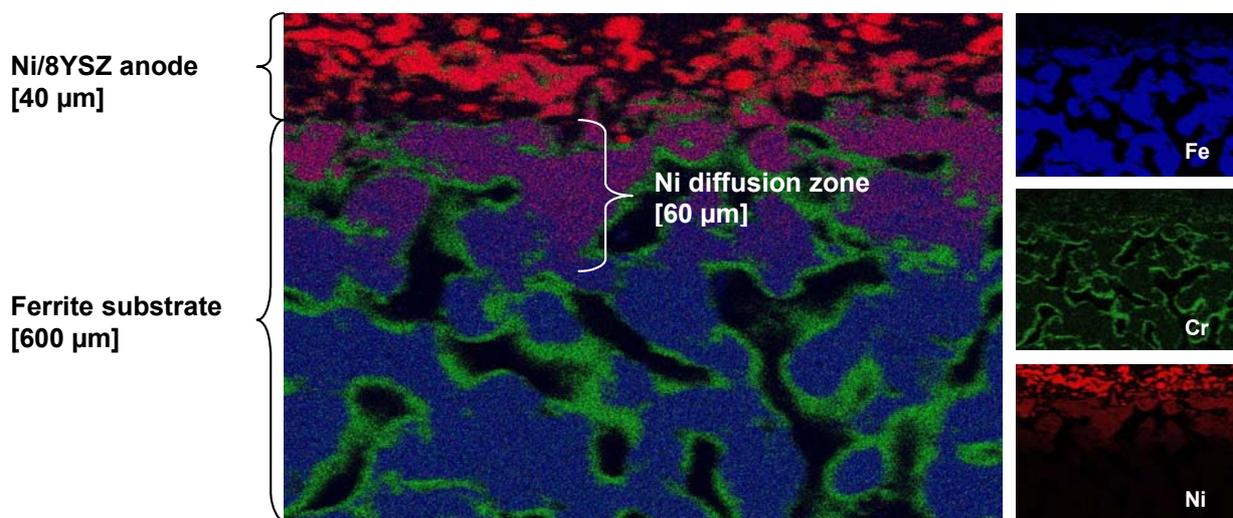


Figure 5. EDX-element map of a Ni/8YSZ-anode on a sintered porous ferrite substrate after 550 hours at 800 °C in Ar-5% H₂-2% H₂O-atmosphere

In the broader sense, it can be assumed that due to the migration of Fe and Cr into the Ni phase of the Ni/8YSZ-anode during long-term cell operation the Ni phase is converted into a Ni-based alloy with relatively high Cr and Fe contents. That means in particular, that the so formed alloy principally shows the characteristic to form thermodynamically stable oxide scales, e.g. NiCr₂O₄ or Cr₂O₃ [15] in the reducing and humid atmosphere of the anode. Hence, the electrochemical activity of the Ni/8YSZ anode is inhibited. This can be seen as a further detrimental effect for fast cell degradation during SOFC operation.

Such detrimental diffusion effects can principally occur in all SOFC concepts in which the anode is directly or indirectly (via nickel mesh) contacted with ferrite interconnects or substrates. Therefore, a solution of this key problem might be interesting not only for plasma sprayed or sintered metallic substrate supported cell concepts (MSC) but also for sintered anode supported cells (ASC). A possibility to solve this key problem could be in the form of an additional diffusion barrier layer on the substrate/anode interface that should exhibit the following properties:

- High porosity for fuel gas access to the anode
- Adapted CTE with respect to the electrolyte ($\alpha = 10\text{-}11 \times 10^{-6} \text{ 1/K}$, 30-1000°C)
- High electronic conductivity in reducing and humid atmospheres ($\sigma = 1\text{-}3 \text{ S/cm}$)
- Chemical stability in reducing and humid anode gas atmospheres
- Barrier effect for Fe-, Cr- and Ni-species
- Electrochemical compatibility to the other cell components at operating conditions
(Inert in chemical respects, especially no reactivity with anode and substrate materials)

Due to the promising experience with the interconnect coatings, the material choice was also directed to the perovskite type materials, in particular to differently doped LaCrO₃-perovskites [16]. Based on dilatometer studies of CTE-values, the temperature dependence of the specific electrical conductivity of potential candidate perovskite materials was measured. Some representative curves are shown in Fig. 6.

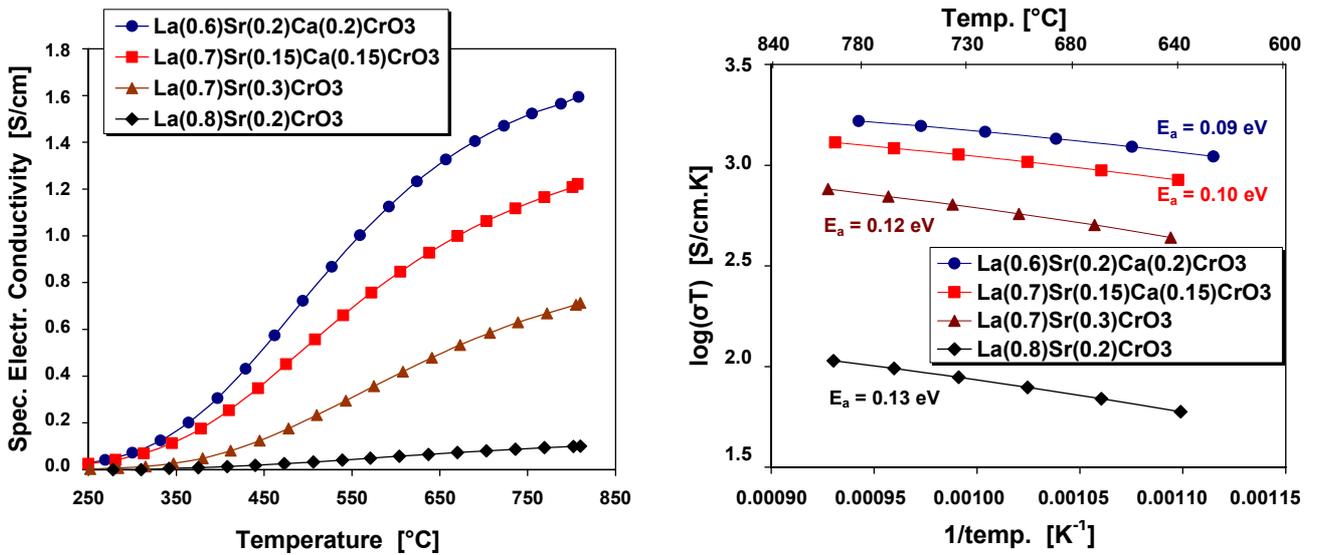


Figure 6. Temperature dependence of the specific electrical conductivity of differently doped LaCrO₃-perovskites measured in Ar-5% H₂-atmosphere (left) and Arrhenius-type plot with calculated activation energies E_a (right)

The above presented stoichiometries show an adequate electrical conductivity (Fig. 6). The compositions La_{0.6}Sr_{0.2}Ca_{0.2}CrO₃ and La_{0.7}Sr_{0.15}Ca_{0.15}CrO₃ show with approx. 1.6 S/cm and 1.2 S/cm the highest conductivities at 800°C and with 0.09 eV and 0.10 eV the lowest activation energies. Compared with the ionic conductivity at 800°C of plasma sprayed (1.62 × 10⁻² S/cm) [17] or tape casted and sintered (3.0 × 10⁻² S/cm) [18] electrolytes, the conductivities of these both compositions are almost two orders of magnitude higher. That promises a relatively low increase of the ohmic cell losses by using these types of perovskites as an additional cell component in SOFC, provided that such diffusion barrier layers are relatively thin and chemically stable.

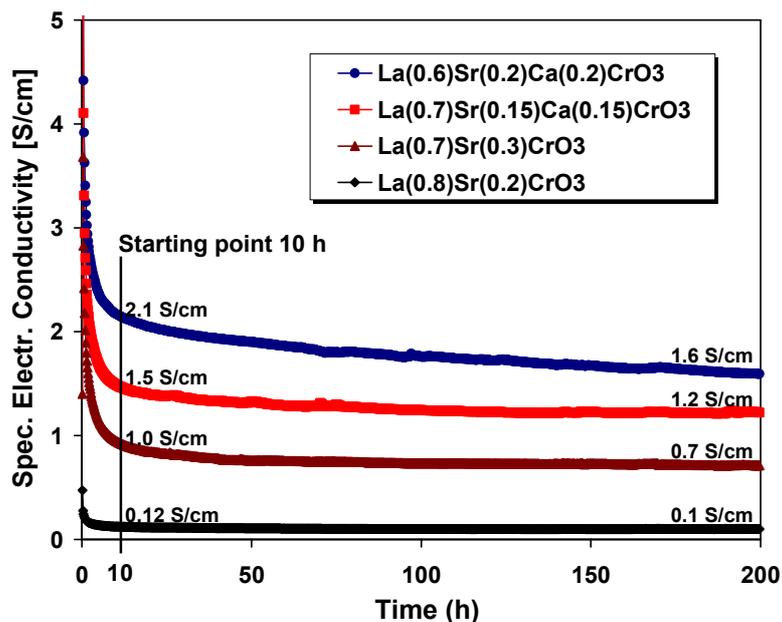
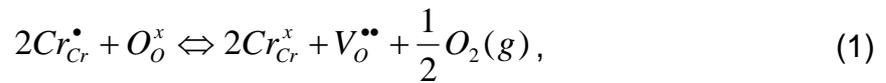


Figure 7. Time dependence of the specific electrical conductivity of differently doped LaCrO₃-perovskites measured in Ar-5% H₂-atmosphere at 800°C

It is well known that during an exposition in humid and reduced anode atmospheres a so called swelling effect can emerge in this perovskites [16] influences directly the electrical conductivity. This can be explained theoretically by the following:

The substitution of trivalent La-ions with divalent Sr and Ca ions with doping the perovskite-type $\text{La}_{1-x}\text{M}_x\text{CrO}_{3-\delta}$ ($\text{M} = \text{Sr}, \text{Ca}$) is compensated by the incorporation of Cr^{4+} on the Cr^{3+} lattice sites. The electrical conductivity in such doped perovskites is generally caused by so-called polaron conduction between the Cr^{3+} - and the Cr^{4+} -sites in the lattice, and hence the conductivity is directly proportional to the Cr^{4+} -content. But in reducing and humid anode gas atmospheres (approx. $p(\text{O}_2) = 10^{-16}$ bar) there is a removal of oxygen from the lattice, and to maintain charge neutrality a fraction of the Cr^{4+} -ions undergoes a reduction reaction to Cr^{3+} that causes a decrease of the polaron conductivity. The defect reaction can be described by the Kröger-Vink notation [19, 20]:



where the subscripts Cr and O label their respective crystallographic sites, and the superscripts \bullet and \times represent a net positive charge and a net null charge, respectively. The V_{O} terms a vacancy on the oxygen site. The change in valence state of the chromium ions and the change in the vacancy concentration are accompanied by a macroscopically measurable volume expansion, the so-called swelling effect.

To investigate this phenomenon time dependent conductivity measurements were performed. Figure 7 shows the time dependence of the specific electrical conductivity of the differently doped LaCrO_3 -perovskites in Ar-5% H_2 at 800°C up to 200 hours. The heating-up procedure from 25°C to 800°C was performed in air to avoid too early swelling effects in the lattice. With reaching the operating temperature of 800°C, the process gas air was switched into the simulated reduced anode gas atmosphere Ar-5% H_2 . After the occurrence of a stationary and stable state the observation of the dependence of the electrical conductivity on time was started. The starting point was at 10 hours operating time.

At first view, it stands out that there is a strong drop down of the electrical conductivity after the gas switch from air to Ar-5% H_2 in the range of 0 to 10 hours measuring time. Corresponding to theory [16], this is a very strong and fast alteration of conductivity caused by the lattice swelling effect that occurred by changing the oxygen partial pressure $p(\text{O}_2)$ from 0.21 bar (air) to 10^{-16} bar (Ar-5% H_2). Furthermore, in the observed measurement period (10-200 hours) the highly doped $\text{La}_{0.6}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{CrO}_3$ -perovskite shows a significant decrease of conductivity from the beginning with 2.1 S/cm till the end of measuring with 1.6 S/cm. This is a relatively strong decrease of the conductivity of 0.5 S/cm in the measurement period. In contrast, the $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ -perovskite shows a decrease of the conductivity of 0.02 S/cm from 0.12 S/cm to 0.1 S/cm during the same time. The other perovskites are in the middle range. Both the conductivity of $\text{La}_{0.7}\text{Sr}_{0.15}\text{Ca}_{0.15}\text{CrO}_3$ and of $\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$ decreases by 0.3 S/cm. This corresponds relatively well with theory [16, 20]. The higher the doping content the higher the electrical conductivity but the higher the swelling behaviour.

However, the present results exhibit an adequate swelling behaviour combined with relatively high electrical conductivity of the four prequalified perovskites. But problems can arise during long-term cell operating conditions.

The above material study was followed by vacuum plasma spray experiments with agglomerated powders shown in Figure 8. These experiments are currently underway. Nevertheless, the results are encouraging, as demonstrated by Figure 9 with the cross-section of a LaCrO_3 -perovskite interlayer between a Ni/8YSZ-anode and a porous sintered ferrite substrate after 250 hrs cell operating time at 800°C with 50% H_2 /50% N_2 and air. During this cell investigation the barrier effect for Fe-, Cr- and Ni-species could be demonstrated.

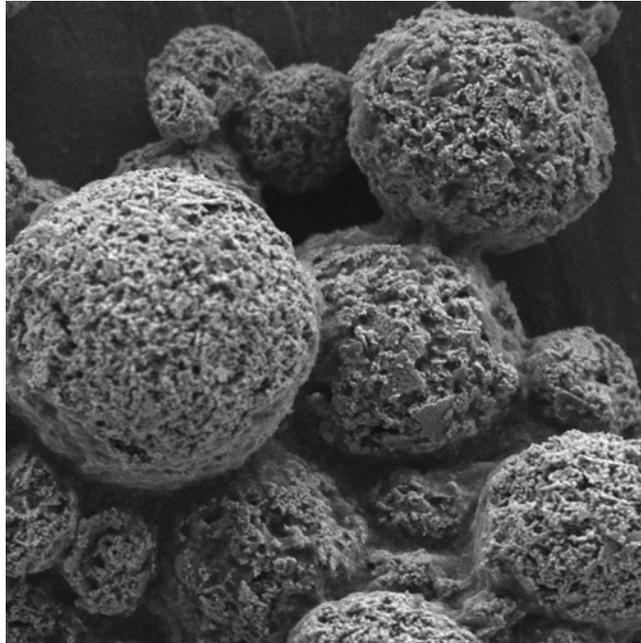


Figure 8. SEM of a typical $\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$ -powder (PSD: $-60+20\ \mu\text{m}$)

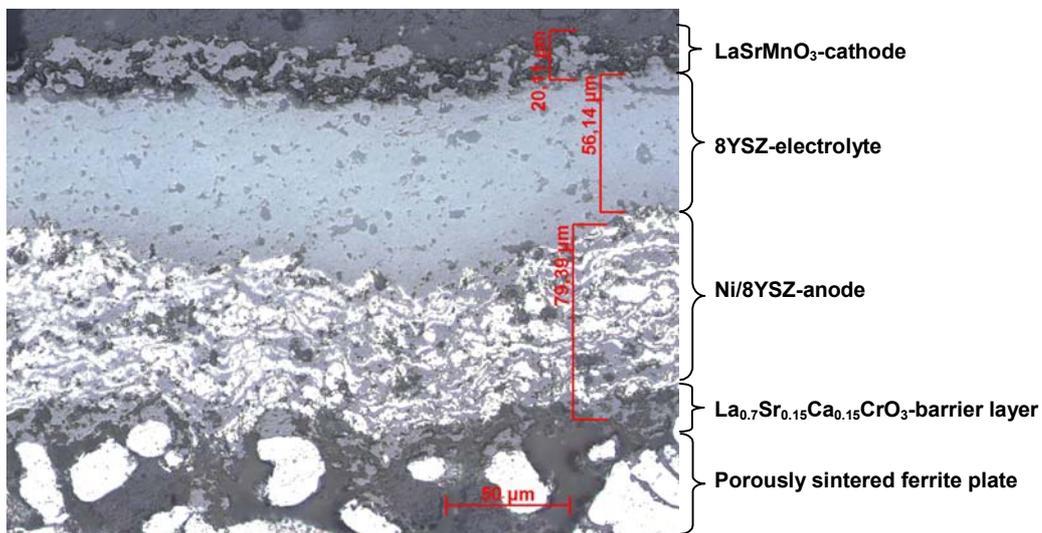


Figure 9. Cross-section of a plasma sprayed cell with LaCrO_3 -diffusion barrier layer between Ni/8YSZ-anode and porous ferrite substrate after 250 hrs cell operation at 800°C

At present, these experiments can be summarized as follows:

- Qualified LaCrO_3 compositions: $\text{La}_{0.7}\text{Sr}_{0.3}\text{O}_3$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$, $\text{La}_{0.6}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{CrO}_3$, 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 for all qualified compositions in short cell operation times (250 hrs)
- Problems can occur with swelling (removal of oxygen from perovskite matrix combined with a volume expansion) of the qualified perovskite-type LaCrO_3

Conclusion

As with the production of the three electrochemically active layers, anode, electrolyte and cathode, and the two additive layers i.e. 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 high velocity vacuum plasma spraying (HV-VPS) with specific powdery precursor materials. In this case, a planar solid oxide fuel cell (SOFC) is built up as principally shown in Figure 10.

Both additive layers promise to reduce degradation effects and hence to extend the life time of such DLR plasma sprayed cells which, at present development state, deliver about 300 mW/cm^2 at $800 \text{ }^\circ\text{C}$ with simulated gasoline reformat as fuel.

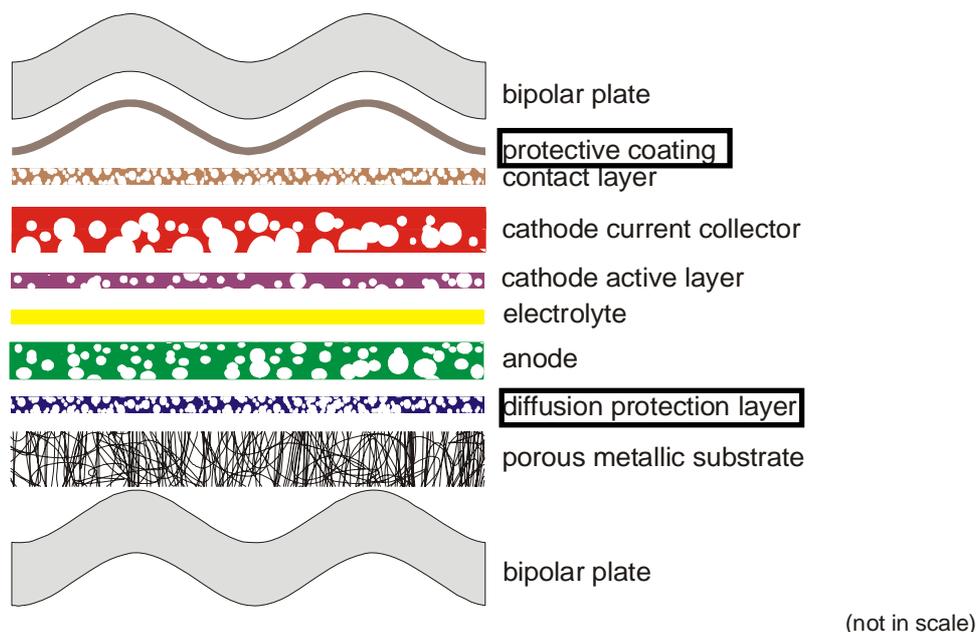


Figure 10. Schematic of the DLR-SOFC-design with the different layers on a metallic substrate

Despite the promising results, further work has to be done to improve the power density, to reduce the degradation effects in order to extend life time, to make spraying of the whole cell more efficient by a higher deposition efficiency process. Furthermore, long term measurements (> 1000 hours) are aimed at in particular to investigate the long-term swelling behaviour and its influence to the electrical conductivity and/or area specific resistance, respectively.

Acknowledgement

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