



Solid Oxide Fuel Cells: A Challenge for Plasma Deposition Processes

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Fuel cells directly convert chemical energy into electrical energy with the potential of very high-efficiency values, because they are not subjected to the Carnot relationship. Of the different fuel cell types in particular Solid Oxide Fuel Cells (SOFC) meet a high interest for different applications due to their specific advantageous properties. They operate in the high temperature range around and above 800 °C and consist in the electrochemical active part mainly of ceramic material. Their economic and technical breakthrough depends still on the success to realize them with high quality, reliability, and efficiency and in particular with acceptable and attractive costs. Different manufacturing methods are in application or under development for the production of the cell components. Beneath these methods are also plasma spray technologies. This review will show the specific demands, the performed and ongoing work, the state of development and especially the required R + D goals to render this type of methods successful.

Keywords Solid oxide fuel cells, function, designs, applications, requirements, production by plasma deposition methods

1. Introduction

The human society is confronted with continuously increasing problems to get sufficient energy to keep or to improve the standards of living for a growing population. This energy amount should be available in a reliable way, to a sufficient volume and at affordable costs without detrimental burdening of environment and climate. Reduction of energy consumption by better equipment and consciousness about the energy situation and in particular by its more intelligent and efficient use are means to moderate this problem. Concerning the latter improved methods for energy conversion, e.g., converting chemical into electrical energy, have to be developed. In these respects fuel cells can play a very important role in future. They are not at all an energy source, but under the precondition that their inherent high theoretical efficiency values—they have not to obey the Carnot relationship because in principle, the thermal energy state is not involved in the conversion process—can be realized to a great extent in reliable, long operating units with acceptable and attractive costs they are like a pseudo-energy source.

As shown in Fig. 1 there exist within the temperature range from about RT up to about 1000 °C several fuel cell types each for a specific temperature range with different

designs and involved materials and they are under development for different preferred application fields.

Fuel cells represent a key technology and an important component for the future energy supply: due to their high efficiency they are able to extend the availability of fossil fuels and because of their potential to use also non-fossil based fuels they widen the field for renewable energy sources.

High temperature fuel cells, to which Solid Oxide Fuel Cells (SOFC) belong with operating temperatures up to about 1000 °C, are of high interest because of their specific properties: They can work with a great variety of fuels—gaseous hydrogen or vaporized hydrocarbons—needing only a relatively low demand for cleaning, in particular concerning sulfur, and reforming of such fuels. Reforming means in this case to generate a usable fuel for the fuel cell, i.e., in the case of SOFCs H₂ and CO from hydrocarbons. The reforming takes place usually at elevated temperature with the involvement of steam and catalytic materials. Another advantage of SOFCs is that the “waste” heat released at a high temperature level can be efficiently used also for a lot of subsequent tasks, increasing thus the overall system efficiency and economy.

SOFCs consist in their electrochemical active part mainly of ceramic materials. Conventionally, for their production methods based on wet powder processing with subsequent sintering steps are applied. But, also a lot of different plasma processes have been used to make material precursors and to deposit materials for cell components or even for entire cells.

The review will describe the principle, typical components and geometries of such cells, the expected applications of relevant systems in stationary, mobile or portable fields and in particular the technological requirements to become attractive for these applications. It will be shown where plasma deposition technologies could be advantageously applied, which relevant activities have been

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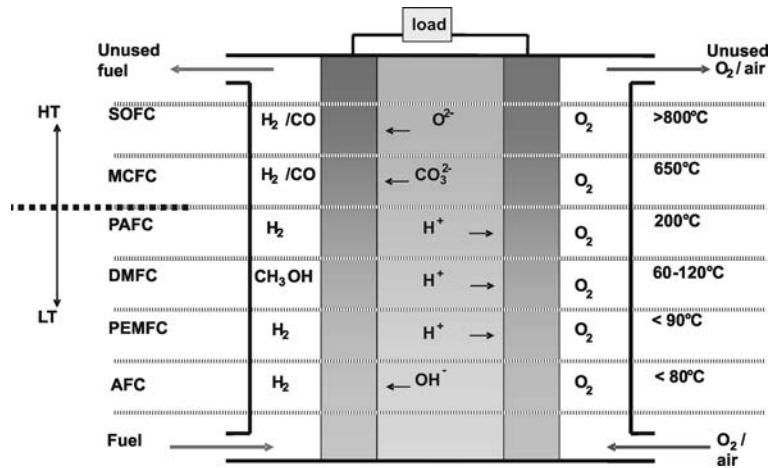


Fig. 1 Spectrum of fuel cell types

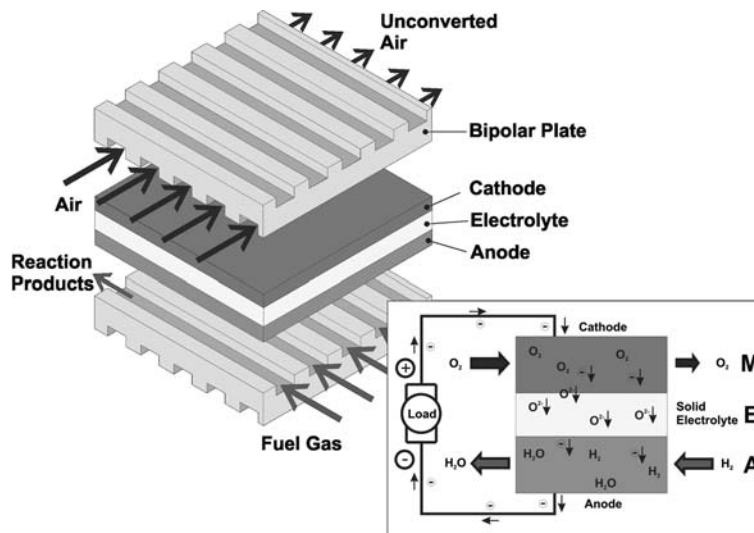


Fig. 2 Principle and function of SOFCs

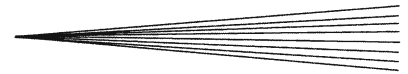
performed, what is going on at present and what is the state of the art already reached in this field. The review concludes with recommendations about further R+D work for improving the situation of plasma deposition technologies for SOFCs.

2. Principle, Function and Main Components of SOFCs

Respecting the main concern of this review only few basics will be given in the following. For detailed information the study of specific literature is recommended, to which belong, e.g., textbooks of Minh and Takahashi (Ref 1) or Larminie and Dicks (Ref 2) for the whole fuel cell

field, and the book of Singhal and Kendall (Ref 3) concentrated on SOFCs. Also the overview about the application of vacuum deposition methods for SOFCs of Pederson et al. (Ref 4) is helpful.

As shown in Fig. 2 with the principle and function of a SOFC (in planar configuration) the core component of cells is represented by the electrolyte which has to be gas tight and only conductive for one type of electrical charge carrier, in the SOFC case for O²⁻-ions. On both sides of the electrolyte the two electrodes, anode and cathode, respectively, are adjacent which are porous to give a good access of the gases—the educts—reacting at the interfaces of electrodes and electrolyte and to dispose the reaction products. In order to guarantee an efficient process these interfaces should be finely structured in the submicron range to get extended three-phase boundaries.



At the interface of the cathode side molecular oxygen supplied by feed air is dissociated and the resulting oxygen atoms are reduced to O^{2-} by picking up two electrons each. These ions migrate through the electrolyte bulk to the anode side. On this side the oxygen-ions react with the hydrogen molecules of the fuel, in the SOFC case with H_2 to H_2O and if CO is present also with this to CO_2 , because CO represents also a usable fuel component with SOFCs.

The reaction products H_2O and CO_2 , respectively, leave the cell with a certain amount of heat. With each reaction two electrons are freed which return via an external load to the cathode side being involved again in the process. Thereby, an open circuit voltage of about 1.1 V is generated. At cell operation producing power this voltage value lies between about 0.5 and 1 V per cell. Current densities amount to values between 0.5 and 1 A/cm². In order to get a technically suitable voltage and power several cells are connected electrically in series to units named stacks, where so-called bi-polar plates or interconnects take care to separate the different gas volumes guaranteeing at the same time a low-resistance for electron conduction.

The usability of CO represents an important advantage of SOFCs in contrast to low-temperature fuel cells like Polymer Electrolyte Fuel Cells (PEFC), where CO is a severe catalyst poison. (With PEFCs a main part of the catalysts is platinum which will be deactivated by a strong CO-adsorption). Therefore, the reforming and cleaning effort is relatively low with SOFCs using standard liquid or gaseous hydrocarbon fuels, e.g., gasoline, diesel, kerosene, heavy oil, or natural gas, respectively, as fuel base. Even hydrocarbon gases gained from bio-materials are considered seriously in recent days.

The cathode materials consist in most cases of mixed conducting oxides of perovskite type, e.g., strontium-doped lanthanum manganite (LSM). The anodes are mostly built as cermets, i.e., mixtures of ceramics and metals are standard consisting of about one-third of electrolyte material to adapt the thermal expansion of the anode to that of the electrolyte and also to extend the reaction domain of oxygen-ions and the fuel. Nickel fills one-third of the volume responsible for high electronic conductivity. About one-third of the volume is represented by the pores. A standard electrolyte material is with yttrium oxide doped and stabilized zirconia (YSZ). With such types of materials the oxygen-ion conductivity increases with rising temperature. Therefore, a relatively high operating temperature is necessary of at least 700-800 °C with YSZ to get a sufficiently high conductivity and attractive power density and efficiency values.

In order to keep the internal losses low the thickness of the electrolyte should be as thin as possible. Another approach in this respect and/or to allow also a reduction of the operating temperature is represented by the use of electrolyte materials with higher ionic conductivity, e.g., scandia doped zirconia (ScSZ) or gadolinium doped cerium oxide (CGO). In some assigned applications such a temperature reduction is of particular interest, not only because it allows for the use of cheaper periphery materials, but also it helps also to reduce degradation effects.

3. Designs, Aspired Applications and Specific Demands

Fuel cells exhibit some very attractive properties, which are mainly the potential for a very high efficiency and the absence of rotating or moving parts in the cells or stacks resulting in negligible noise and low-maintenance expenses. Also, their modularity is advantageous. This means that the desired power level of a fuel cell system can—to a certain degree—be arranged by putting together an adequate number of identical elements. This renders the development cheaper and also allows in principle the replacement of a failed cell.

Due to their attractiveness numerous SOFC development activities are under way world wide devoted to different types and geometries of SOFCs for a wide range of power levels and considered applications. This involves:

- Small portable systems with some few hundreds of watt in particular for military applications.
- Systems in the power range of about 1-5 kW, in stationary version for domestic heat and power generation and as mobile type, mostly devoted for Auxiliary Power Units (APU), which enjoys increasing interest, at present.
- Medium sized systems with a power range of about 10-50 kW or even higher for decentralized stationary CHP (combined heat and power supply), where the use of bio-material based fuels is increasingly considered.
- Large systems in the range from about 100 kW up to several MW, where also CHP with stationary power units of utilities are being considered.

Depending on the projected application and power range different cell and stack geometries are favored.

3.1 Small Tubular Cells for Portable Systems

For systems in the very low power range small tubular cells are under development where these tubes have an outer diameter of only few mm, a wall thickness of about 1 mm and an active length of some cm. A considerable number of such cells have to be put together to stack modules. The big advantage of these small tubular cells, mostly consisting of yttria stabilized zirconia, is the tolerance for high thermal gradients and transients, i.e., they can be heated up to the operating temperature within only few minutes. One of the pioneers developing such small tubular cells is K. Kendall (Ref 5, 6). Encouraging results with this technology were reported (Ref 7, 8), recently. Figure 3 shows several cells arranged to a stack module (Ref 7).

3.2 Cells for Low Power Range Systems

For this power range of about 1-5 kW mostly planar cells are under development. Besides, also some activities use tubular designs. In the latter approach the performed activity of the former Canadian company Fuel Cell Technology (FCT) with shortened SOFC tubes of Siemens



Fig. 3 Bundle of small SOFC tubes for 200 W, operated at $\sim 800^\circ\text{C}$ (Ref 7)

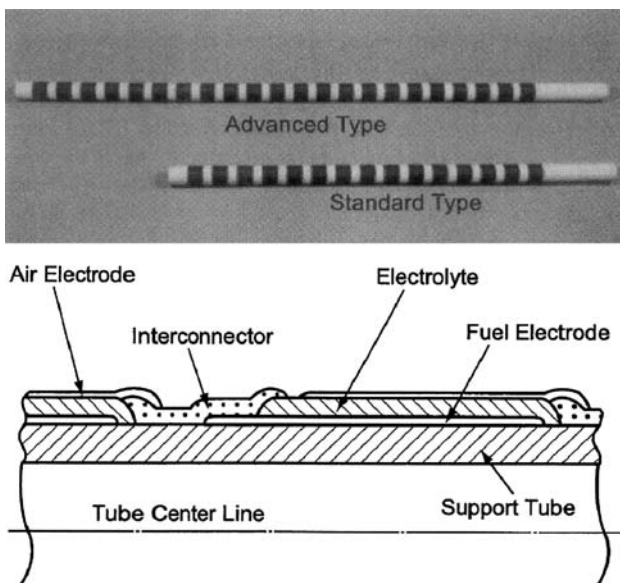


Fig. 4 Former Bamboo type cell of Mitsubishi Heavy Industries (Ref 9)

Power Gen (SPG)—former Siemens Westinghouse Power Corp. (SWPC)—(see also section 3.4) and the former “Bamboo-Design” of Mitsubishi Heavy Industries (Ref 9) should be mentioned (see Fig. 4).

A fuel cell assembly with “Bamboo-Design” components consisted of porous electrically insulating ceramic support tubes of about 20 mm outer diameter where on each tube several short cell rings were positioned made by plasma spraying to generate with each arrangement

several volts. But for this low power range, for several reasons now mostly planar designs are favored, and for these designs metallic interconnects are preferred which provide several advantages compared to former ceramic interconnects. But also certain problems have to be encountered. Some typical activities with planar designs where plasma production technologies are considered shall be described in the following, shortly.

3.2.1 Portable SOFC Generator with Methanol. On the 7th European SOFC Forum in Lucerne 2006 a paper was given about the development of a portable 1 kW SOFC generator with 25 circular cells of 110 mm outer diameter operated with methanol where Vacuum Plasma Sprayed (VPS) components and cells are also under consideration and test (Ref 10). Such generators shall supply in a ‘clean, quiet and reliable way power for cottages, recreational vehicles, mountain resorts, homesteads, water and ground vehicles, or even for military applications, police or rescue operations.’

3.2.2 Small Stationary Systems. A big amount of work has been devoted by Sulzer HEXIS AG, now HEXIS AG, in Switzerland to the realization of micro-CHP systems with about 1 kW of electricity and several kW of heat for single family homes (present product name Galileo 1000 N). Figure 5 depicts the principle of the cells used in this “open” design. The fuel is fed centrally, and because of the fact that the rims of the circular cells are not closed the un-used fuel is burned in the surrounding of the cell producing useful heat. Such a design avoids some otherwise existing problems particularly concerning insulation and sealing. But it means also relatively low fuel utilization for electricity generation and some “redox” problems in the rim area where oxidizing and reducing conditions can exist the same time. The backbone of the cells are contoured interconnects consisting of ferrite materials with high-chromium content (Ref 11).

With similar applications in mind, i.e., domestic CHP, but with a little bit higher power level the Canadian activity, mentioned above and stopped in the meantime, was pursued.

3.2.3 Small Mobile Units. In recent years the interest for the use of SOFC systems in the power range of about 1-5 kW has been impressively increased, in particular for the use as Auxiliary Power Units (APU). The term APU comes from aircraft “Auxiliary Power Units.” These are on-board electrical power supplies operating independently from the main engines and consist mostly of relatively small gas turbines, which use favorably the on-board fuel. The electricity of APUs is predominantly needed on ground for air conditioning and other functions when the main engines are not in (full) operation. Such APUs show a relatively low efficiency and cause a considerable amount of exhaust, noise, and maintenance effort. These drawbacks of present aircraft APUs are the reason why there exists in this field a great interest and some activity for alternatives, e.g., for fuel cell systems, promising higher efficiency, reliability, and hence acceptability (Ref 12, 13).

Rapidly increasing need for electrical power characterizes the progress in modern cars. Since the introduction

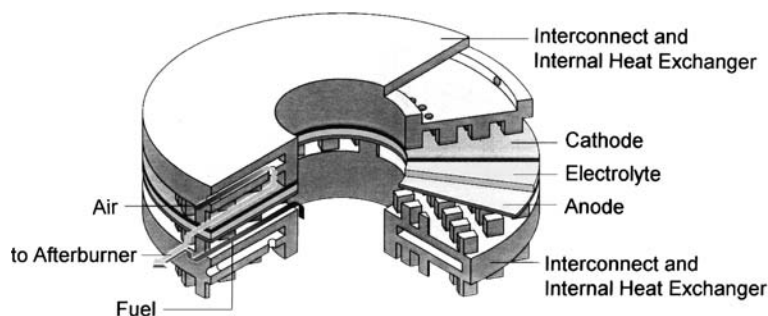


Fig. 5 Principle of HEXIS SOFC design (Ref 11)

of generators in cars—at that time only responsible for illumination—the electrical power has increased by about 500% and the battery capacity by about 200%. Nevertheless, there are still more desires or needs for more electrical components on board, but a further increase of these generators, operated and mechanically coupled with the main engine—in most cases an Internal Combustion Engine (ICE)—cannot be recommended due to economical and efficiency reasons, particularly when ‘stop and go’ characterize the car operation. Therefore, there is a great interest to have an ICE-independent power source which would allow replacement of a lot of present components by better controllable and more efficient electrical ones and to optimize both functions—traction and electrical power. This would increase economy and safety of cars. Also idling would no longer be necessary to have electricity, e.g., for air conditioning. Such a source would considerably reduce the ICE operating hours, the fuel consumption and hence the waste release. In this respect SOFC-APUs seem to be very attractive, because they are able to operate with standard car fuels needing only a relatively low effort for cleaning and reforming of these fuels.

Representative for the goals of car manufacturers interested in SOFC-APUs the target values of BMW for passenger cars to be found in (Ref 14, 15) will be given as follows:

SOFC system power	6 kW _e /42 V
Power density of the cells	>0.5 W/cm ²
Specific weight of the stacks	<4 kg/kW _e
Operating temperature	~800 °C
Fuel	Reformat of gasoline or diesel
Start-up time	<10 min
Overall operating time	>5000 h
System costs	<500 €/kW _e

Figure 6 shows one of the first realizations of such planar cells where the electrochemical active part was made by plasma spraying (Ref 16). How they are principally stacked together is given in Fig. 7. Details are described later on in section 5.7.

Such APUs could find a great field of application, e.g., in trucks, buses or refrigerator cars, because idling will be more and more limited by law in populated areas. Similar

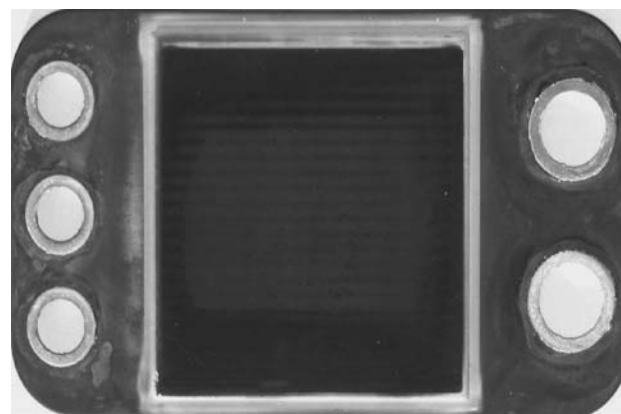


Fig. 6 Cassette cell with plasma sprayed SOFC

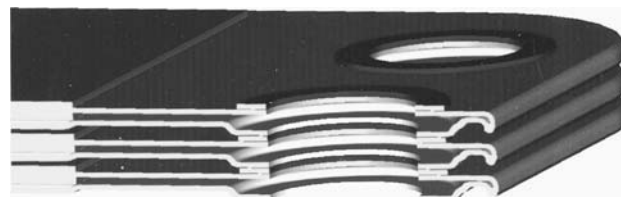


Fig. 7 Principle of cassette cell stacking for mobile application

conditions appear also in the marine field with leisure boats. An interesting issue are electrical vehicles which, at present, have only limited attractiveness particularly because of their short operating range and the heavy batteries needing long times for recharging. A permanent operating SOFC-APU fed by gasoline or diesel could continuously charge the battery and hence increase the range and therefore the market of such Electric Vehicles (EV) which simultaneously could be considerably lighter (Ref 17).

Also the main civil aircraft manufacturers Boeing and Airbus are involved for several reasons in the development of APUs. But, in this connection very specific operating conditions have to be addressed: for instance, besides high reliability, the problem of fuel contaminants like sulfur in standard kerosene and the operating situation at cruising altitudes:

- There, the oxygen partial pressure is only about 20% of sea level, therefore means have to be developed to give the fuel cell sufficient oxygen and
- The ambient temperature is typically below ~ -50 °C.

3.3 Medium Sized Stationary Systems

Under the precondition that the APU-cells and—stacks can be successfully developed there will be the chance to combine several of these stacks to systems with a power of some tens of kW, which can become attractive for decentralized CHPs (Combined Heat and Power) using for instance biomass based fuels, which seems to gain great importance as future energy supply.

For higher power levels in the 100 kW-range the SOFC-systems of Siemens Power Gen., have to be considered presently as first options. They have the longest continuous development history and the closest approach to technical application. Several systems, pressurized and non-pressurized, have been tested, showing very low degradation at considerably long operating time. Despite the high-development state there are at least two fields where further progress is needed with this SOFC-type: power density and production cost.

In the first design the cells have been of tubular shape, almost two meters long and about 2 cm in diameter (Fig. 8). The tubes are closed at one end and consist mainly of a cathode of perovskite type material on which the thin electrolyte, the anode and an interconnect strip for electrical connection with the next cell are put on. The outside is therefore the anode side being in the fuel surrounding whereas the air is fed to the tube inside. A main advantage of such cells is that the separation of air and fuel volumes is easily to manage, but the low power density and the high specific amount of expensive cathode material are disadvantageous. In order to increase the volumetric specific power density and the efficiency and to reduce the material costs new designs named HPD (High Power Density) and Delta are under development as shown in Fig. 9 (Ref 18).

In the first development period the thin electrolyte of yttria stabilized zirconia was produced by Electro Chemical Vapor Deposition (EVD) starting from the chlorides of zirconium and yttrium reacting with oxygen on the cathode surface forming a very dense electrolyte of high quality. But the process takes long hours and is costly, in the meantime this process could be replaced successfully by the much cheaper Atmospheric Plasma Spraying (APS), where a thermal after-treatment guarantees a sufficient density. Also the interconnect strips of lanthanum chromite are made by APS. Flower (Ref 18) emphasizes in his paper: 'Atmospheric plasma spraying is fully qualified as a mass manufacturing technology—many thousands of cells have been produced.'

3.4 Large SOFC Systems

With further improvements concerning performance increase and cost reduction 'Siemens PG is focused with

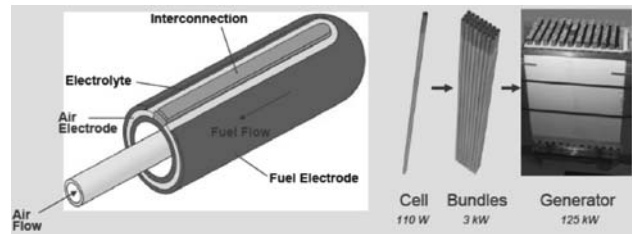


Fig. 8 Tubular SOFC design of Siemens PG

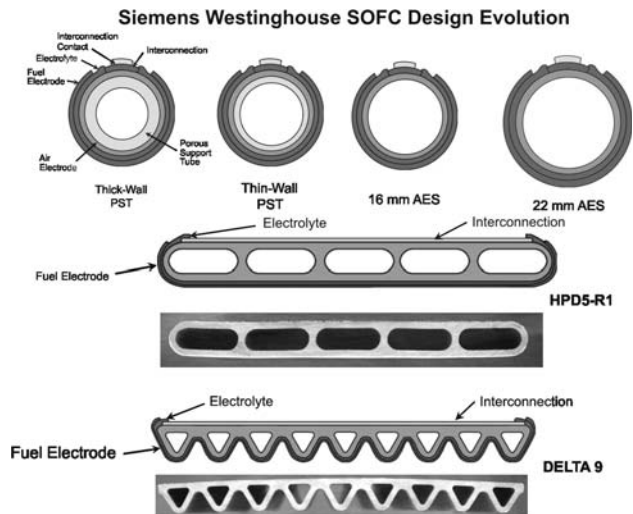


Fig. 9 Evolution of Siemens PG SOFC design (Ref 18)

its SOFC on the so-called industrial and dispersed markets characterized by ratings in the order of 500 kW and 2 MW, respectively' (Ref 18).

In competition Rolls-Royce follows its own concept with ceramic tubes of rectangular cross section (see Fig. 10) on which the cell components are put on as planar strips by wet powder techniques and sintering. Several cells are series connected on each insulating support. (Perhaps plasma processes could become interesting with further improvements). For more details see the paper of Travis et al. (Ref 19).

Thinking about large SOFC systems, it has also to be taken into consideration, that with Molten Carbonate Fuel Cells (MCFC), operating at temperatures of about 650 °C, impressive progress has been obtained in the last years, showing its advantageous properties already with fuels of renewable energy sources (bio-materials).

4. Main Requirements to be met by SOFC Components and their Production

The overview above has shown that there are a lot of different applications with different power levels for which SOFCs are under development with adapted designs and sizes. But, despite of all the differences there are several common requirements concerning quality of cell and stack components and also concerning their production.

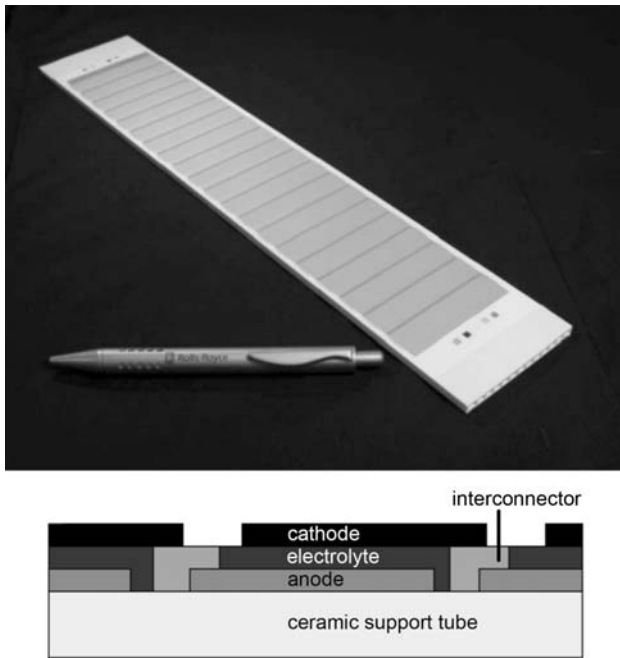
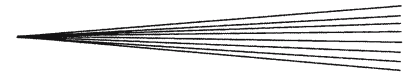


Fig. 10 SOFC fuel cell technology of Rolls-Royce (Ref 19)

4.1 Quality Requirements

General demands are:

- *High efficiency with high fuel utilization at high area and volume specific power density.* This means in particular (1) low-internal ohmic losses, (2) efficient electro catalytic activity of the electrodes having a sufficient porosity for access of the reacting gases and for the release of the reaction products, (3) thin, but dense electrolytes of materials with high-oxygen-ion conductivity, (4) fine-structured interfaces between electrodes and electrolytes, where a graded material and porosity transition among the different cell components is advantageous.
- *High lifetime despite the high operating temperature,* i.e., high stress tolerance, which means compatibility of the different materials with respect to their thermal expansion (CTE) and low degradation by avoiding the formation of detrimental phases caused by material migration due to inter-diffusion or material evaporation and deposition at critical areas. Also structure coarsening and reactions with fuel contaminants (e.g., with sulfur) or condensation of fuel components (carbon) have to be avoided. It has to be mentioned that the reduction of operating temperature is one option to reduce degradation effects and hence to increase lifetime, but there is a certain temperature level needed to have a sufficiently high oxygen-ion conductivity (low ohmic resistance) of the electrolyte materials. Therefore, the use of electrolyte materials with higher ionic conductivity compared to YSZ, e.g., ScSZ (scandia stabilized zirconia) or CGO (gadolinium doped ceria) are options. Also, the development of electrolytes as thin as possible is under way.

- For certain applications relatively long lifetimes of cells and stacks are required at very challenging conditions in particular in the case of APUs for passenger cars, where very short start-up times are required meaning a fast heating-up and strong temperature gradients and transients. Also, with this application the anodes can be stressed by redox processes (oxidative and reducing conditions), where the nickel in present-type anodes will react numerous times to its oxide and back to the metal state which is in each case combined with volume changes weakening the anode structure.
- *Acceptable and Attractive Costs of Production Technologies:* Of course, fuel cell systems have very attractive properties, in principle, not only due to the high inherent conversion efficiency, but nevertheless, their costs have to be in a certain limit to become competitive or superior to now-a-day systems. This issue concerns both materials and way of production.
- *Materials:* They have to be reasonably cheap and sufficiently available, in particular when larger amounts are needed for mass production. Expensive materials should be avoided as far as possible or only used in low concentration for doping or as very thin layers. In the case of APUs for cars in particular considerable cost reduction are a main challenge. There, specifically developed ferrite steels in the shape of thin sheets for the cell cassette and as interconnects seem to open the chance, not only due to the CTE which is more adapted to the value of the electrolyte, but also, as consequence of these advantages some new problems have to be solved with this approach; more about later on.

4.2 Production Process

A general demand on the production process is the ability to generate the desired product quality together with the availability of the materials for the product in appropriate quality (size and purity). The process should show a high yield and productivity. Also, it should be suited for automation and for mass production allowing for reproducible manufacturing. Resulting “wastes” should not be toxic and not expensive to dispose. They should be recycled as far as possible.

Conventionally, SOFC components and entire cells have been made by processes which can be summarized under the topic “*Wet Powder Processing*” including Tape Casting, Screen Printing, and Sintering Steps. The relatively new process family, representing the topic of this article, can be characterized by *Deposition Processes Making Use of Thermal Plasmas*, e.g., plasmas generated by DC and RF discharges either for spraying of powders or for synthesizing and subsequent deposition of materials.

Comparing both process families it can be stated in a simplified way, that the

- *Wet Powder Processes* are well-established and relevant equipment and knowledge is available, in principle. But, these processes need high-process temperatures for relatively long periods which can

cause material and structure alterations and which limit material selection particularly for the substrates.

- *Plasma Processes* are relatively new, needing still much more development work. Processes to get the desired quality and equipment for mass production have to be developed further. Also a lot of investment capital is needed to build the production equipment. But, there are several important “pros”: These processes are fast, no or only slight postprocessing of the product is needed, in general. A large variety of materials (also new ones) can be processed to efficient layers and components with controlled composition and porosity. The thermal load due to deposition is relatively low and short, therefore also cheap substrate materials, i.e., ferrites, can be used.

5. Activities and State of the Art Using Plasma Technologies for Production of SOFC Components

5.1 History of Plasma Technologies for SOFCs

Forty years ago, first approaches took place to use thermal spraying for producing the electrodes-electrolyte assembly of SOFCs as documented by a Swiss patent (Ref 20). In this connection, a further patent has to be mentioned (Ref 21) also. The same authors (Gruner and Tannenberger) claimed in 1990 and in 1994 that with the Vacuum Plasma Spraying (VPS)-process the possibility was opened-up for a one-technology fabrication for the entire cell without breaking the vacuum, where the pressure was about 100 mbar (Ref 22, 23).

They measured a maximum power density of 230 mW/cm², (160 mW/cm² at the standard voltage of 0.7 V), at an operating temperature of 910 °C with an active cell area of 4.5 cm², applying humidified H₂ as fuel. A porous Ni-zirconia cermet served as anode. The electrolyte was made of yttria-stabilized zirconia, the porous cathode of LaSrMnO₃. In order to guarantee the required gas tightness the electrolyte thickness was 250 μm which is relatively high, causing considerable internal polarization losses. Another draw-back, to present knowledge was the use of a Ni-felt as cell-support where redox-problems and the mismatch of the Coefficient of Thermal Expansion (CTE) to the electrolyte resulting in cracks were probably the reason for a very high power degradation of about 10% within 600 h. Gruner and Tannenberger reported also already in 1990 that the chemical and crystalline nature of the spray material will not be changed during the process if specific spray parameters are applied (Ref 22).

Mallener et al. (Ref 24) reported a progress in making more efficient SOFCs by an adapted VPS-process, but they observed problems to spray cathode material without some decomposition effects. A further step forward producing and developing SOFCs using VPS was reported in 1994 by Henne et al. (Ref 25). They applied Laval-like contours of the DC plasma torch anodes (Ref 26) (Fig. 11,

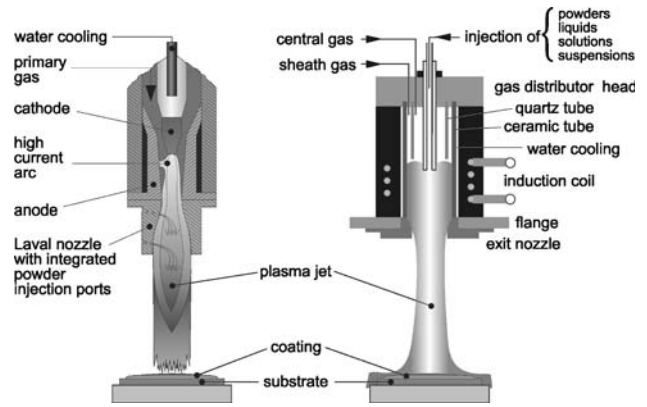


Fig. 11 Principles of DC and RF plasma spray torches applied at DLR (Ref 26, 27)

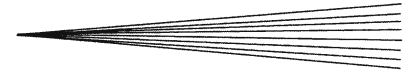
left) and maintained supersonic pressure conditions where very fast plasma jet and spray material velocities with very short interaction times of the spray material with the hot plasma can be obtained resulting in very dense, but not yet fully dense electrolyte layers. Furthermore, by using oxygen as feed gas even very thermally sensitive oxides could be deposited almost undecomposed as cathode layers. With these experiments also further advantages with such supersonic nozzle contours appeared as consequence of the fact that the spray distance could be enlarged and the plasma jet extended reducing thereby the local thermal load on the substrate by increasing the spray spot (Ref 26).

In the meantime a lot of further articles appeared showing the progress concerning processing of SOFC materials, the relevant plasma processes and the obtained results with cell components and with entire cells, as well, which will be described partially in the following.

5.2 Production of Electrolytes

Electrolytes for SOFCs require the highest demand on quality and production. They should be very thin in the range of some μm up to few tens of μm to keep the internal resistance for conducting the oxygen-ion low, but still being dense enough for avoiding the permeation of reacting gases which would not only reduce the performance, but, also in the case of H₂-transfer lead to H₂O-formation at the cathode side causing increased degradation effects by destroying the cathode with time. Also, a well-developed fine-grained structure at the interfaces to the two electrodes with graded material and porosity transition showing an extended three-phase boundary zone should exist.

Plasma spraying is blamed for its drawback that the production of fully dense ceramic layers is almost impossible with it, and particularly, as already described, when most present SOFC-electrolytes consist of relatively high melting ceramic materials, e.g., Yttria Stabilized Zirconia (YSZ). Nevertheless, means have to be developed to make those layers as dense as possible either by process improvement or by postprocessing.



Concerning the latter in some cases densification of the sprayed layers by postsintering is permissible. One prominent example represents the Siemens fuel cell technology with the long SOFC-tubes (Fig. 8) consisting mainly of ceramic (perovskite) cathode material on which the YSZ-electrolyte is sprayed by Atmospheric Plasma Spraying (APS). With a sintering temperature somewhat above 1200 °C sufficiently dense electrolytes can be produced. But with this postprocessing it has to be taken care that the finely structured interface zone between cathode and electrolyte made by a wet powder process will not be destroyed.

In other cases such a thermal postprocessing is not allowed or only at considerable lower temperatures. In such cases the generation of highly dense coatings by the spray process is even more necessary. There are several approaches to get improvements. One is the use of very fine-spray powders. Usually, with VPS of YSZ a grain size fraction of $-22.5\ \mu\text{m}$ and $+5\ \mu\text{m}$ is used. A further reduction of the grain size will increase the costs particularly with fused and crushed powders and also problems with powder feeding will rise. A further lowering at the finer end of the fraction can also result besides injector clogging in increased evaporation of the fine share and in low-layer quality and Deposition Efficiency (DE). Depending on powder morphology there are limits somewhere around $5\ \mu\text{m}$. Only a narrowing of the grain size distribution—which means increase of powder cost—may be helpful because an optimized setting of the spray parameters would be easier. Concerning the powder morphology it turned out that in contrast to first opinion fused and crushed powders revealed superior in DE and layer quality over agglomerated ones which consist of very fine constituents. Perhaps these fine constituents freed by decay of the agglomerates will evaporate and cool down before hitting the target, or will not attain enough inertia to hit and to spread on the target to produce a dense coating (Ref 28).

Recently the use of suspensions came into consideration in order to make very fine-particles suitable for processing. Such particles can be produced to reasonably low-cost by chemical processes. With some success such suspensions have been applied with DC-torches in atmosphere (Ref 29, 30). With such suspensions the liquid has to be evaporated in the first step within the plasma jet before the melting of the solid particles takes place. But, concerning APS the spray distance has to be very short (40-60 mm are reported in these articles) and therefore, local overheating of the substrate could take place together with strong thermal gradients and transients at the necessary movement of the plasma source over the substrate to coat it fully. Therefore, the coating of technically interesting large substrates without the appearance of cracks could be difficult. More relevant development is recommended, because also the porosity values reported in this article with more than 20% are by far too high to be acceptable for technical SOFCs.

Siegert et al. reported in 2004 about their work to get dense electrolytes. In this context also information was given about the influence of the main operating parameters,

e.g., suspension velocity modes on coating density (Ref 31). They used a suspension of sub-micron YSZ-particles in ethanol. As plasma sources both Sulzer Metco F4 and Triplex were applied in atmosphere. The deposition efficiency values were about 50%. The operating parameters had a strong influence on density where density values over 70% could be obtained. But still, this is not sufficient for SOFC requirements.

As mentioned above local overheating of substrates represents a severe problem with plasma spraying of SOFCs. Therefore, means have to be applied with which the cross section of the plasma jet is extended in order to reduce the thermal load. This requires special nozzles for the plasma source and adapted parameter conditions. Also the spray distance has to be enlarged, where nevertheless the spray material should stay hot enough to hit the target in molten state. One possibility to meet these demands is to spray in an environment with reduced pressure and with nozzles (see Fig. 11, left) allowing for supersonic plasma jets when a sufficient pressure gradient between the plasma source and the spray reactor exists. DLR has long experience with the design of supersonic nozzles for VPS and its application for SOFCs (Ref 25, 26). Such nozzles with certain modification are also advantageous for APS (Ref 32).

With VPS as similar with APS such nozzles can generate an extended hot cross section of the plasma jet where more powder particles are becoming involved. This means a higher Deposition Efficiency (DE), reduced peak temperature in the jet center and lower local thermal load for the substrate. The jets show reduced gradients at the rim. Also the cold gas entrainment is delayed. The extended spray area allows for a better overlap at scanning over the substrate. With VPS further improvements can be added as are higher plasma jet and spray material velocity resulting in denser coatings, reduced entrainment effect and the advantage for extended spray distance reducing further thermal loads and gradients. Recently also the advantages of shrouds for APS could be demonstrated (Ref 33).

With all the DLR experiments producing electrolytes with VPS it turned out that preheating of the substrates to about 400 °C (mean temperature between ambient and operating condition of the SOFC) revealed advantageous not only due to a better match of the stresses, but also by reducing temperature gradients and transients within the substrate. Also heat conduction from the molten spray material droplets to the substrate is better, which means an improved flowing and bonding and increased DE, as well. This can be explained at least partially by the removal of adsorbed water films on the substrate surface by temperature (and vacuum). Such films have a negative effect on material bonding and spray material flow because vapor barriers can be generated.

A lot of work for SOFC using VPS has been performed at DLR up to now, where, depending on the metal of the porous substrate—knitted wire of ferrite steel or Ni-felt—power densities surmounting about 0.25 and 0.35 W/cm², respectively, could be obtained at 800 °C with simulated gasoline reformat (Ref 16, 34-36). Nevertheless,

further improvements concerning the electrolyte quality are urgently needed to cope with sintered cells. Despite the considerable improvements in the past the electrolytes are still not dense enough and with the presently applied standard plasma sources, e.g., Sulzer Metco F4 even with high-velocity nozzles the spraying takes place close to the power limit of the torch. With such plasma sources a further power increase for better melting and acceleration of the spray material must, therefore, be limited because of the problem of local substrate overheating. In the case of a plasma source with higher power an extension of the plasma jet and/or the spray distance is of course necessary which is favored for operation in an environment at reduced pressure.

With the topic of making improved electrolytes the reading of some papers with special approaches and information has to be recommended here.

In the paper by Renouard-Vallet et al. (Ref 37) the authors describe that the electrolyte porosity controls not only the mass of gas diffusion, but, together with the quality of the internal structure of the lamellas also the oxygen-ion conductivity and hence the internal polarization losses. For APS and VPS the relationships between spraying conditions and the in-flight properties of the particles upon impact were studied in addition to the resulting coatings. It turned out that in general the oxygen-ion conductivity of optimized VPS-YSZ-layers overcame the values of APS-produced layers and that a rise of the substrate temperature also improves the conductivity due to better inter-lamellar contacts.

Using a D-optimal design of experiments (DOE) the influences of powder feedstock and of plasma gases were examined by Syed et al. on deposition efficiency, gas tightness and electrochemical behavior of vacuum plasma sprayed YSZ for SOFCs using in particular in-flight measuring equipment. This has led to improved electrolytes (Ref 38).

In order to get denser and better internally bonded electrolytes recently the idea came up to add small amounts of transition metal oxides to allow for a sintering at considerably reduced temperatures (Ref 39). Following to this idea it should be studied if this procedure can also be applied with success with plasma spraying of electrolytes, either directly with the deposition process or with an acceptable postprocessing technique where preferably the use of the plasma jet itself would be advantageous for reasons of process simplification.

Li et al. (Ref 40) reported a successful densification of APS-sprayed YSZ electrolytes by repeated infiltration of zirconium and yttrium nitrate solutions followed by baking processes at 500 °C for complete decomposition of the nitrates.

Concerning the densification of electrolyte layers and the improvement of layer structure and inter-lamellar bonding of YSZ by transformation of a lamellar morphology to a granular microstructure Khor et al. applied with success spark plasma sintering of plasma sprayed YSZ. Starting with an initial porosity of about 10% a value a little bit above 1% could be obtained, and a processing time of only 3 min was sufficient (Ref 41). Unfortunately,

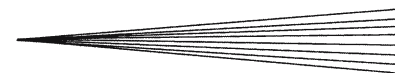
the recommended 1400 °C as process temperature will only be usable for limited applications. Starting with a layer of considerably lower porosity this process temperature could perhaps be reduced to an acceptable temperature level. With the information described above further activity to get denser electrolytes with better internal bonding (higher oxygen-ion conductivity) should also be directed toward more powerful plasma sources. With this concern High Frequency Pulse Detonation (HFPD) was also tested as thermal spray process concerning the relevant potential, in the meantime. Highly dense (>98%) and hard coatings could be obtained with fused and crushed P-YSZ ($ZrO_2 + 7 \text{ wt.} \% Y_2O_3$) powder in atmosphere with a stand-off distance of 40-80 mm, respectively (Ref 42). (P-YSZ means partially phase stabilization of zirconia by yttria).

A considerable progress promises the approach with the LPPS (Low Pressure Plasma Spray) Thin Film Process using the O3CP-torch of Sulzer Metco (Ref 43). With this torch the plasma jet exits through a contoured nozzle in a vacuum surrounding of less than 10 mbar. The torch can work with a power up to about 180 kW and at an extended vertical spray distance well above 1000 mm the deposition area can cover more than 0.5 m². In this way the spray pattern is enlarged reducing thermal gradients and promising a more homogeneous material deposition. It is reported that at a chamber pressure of 1.5 mbar and an input power of 125-150 kW with a powder feed rate of 90 g/min a typical deposition efficiency of 40-45% can be obtained. The torch can be rapidly moved and the spray plume passes therefore very quickly over the substrate to control the heat load. Typically, about 1 μm is deposited per pass. According to the report 50-60 μm are necessary to get a dense electrolyte. If postsintering is allowed the required layer thickness for the necessary density could perhaps be reduced toward 30 μm. Unfortunately, no results of electrochemical tests with such SOFCs are available at present.

Radio Frequency (RF) plasma spraying (also known as Induction Plasma spraying, RF-ICP) applied in a reduced pressure environment seems also to be promising because the spray material (powder, suspensions or liquids for plasma synthesis) can be centrally injected (Fig. 11, right), not more or less in radial direction as with standard DC equipment. This means better process conditions, in principle. Also higher spray material inertia with less material evaporation due to higher velocity is possible due to shorter dwell time. With larger spray distance also a reduced area specific thermal load can be obtained.

In the paper of Mailhot et al. (Ref 44) the influence of the different process parameters on porosity with supersonic induction plasma spraying of yttria stabilized zirconia films was investigated, showing the potential of this process-type for producing dense SOFC electrolytes, because densities of more than 98% could be demonstrated. In a recent paper of Renouard-Vallet et al. (Ref 45) further progress with this process-type was reported.

As already mentioned this process type is relatively recent and not yet fully developed. Therefore, further work should be performed to reduce the problem of



clogging within the notch of the RF-torch and to diminish further local overheating of substrates by better thermally controlled process equipment.

For certain applications in mind the SOFC-activities are directed toward lower-operating temperatures. In this connection the paper of Jia et al. (Ref 46) deserves special attention, because it gives some interesting insights about the preparation of precursor solutions, the induction plasma spray process with supersonic TEKNA nozzle itself and the influence of the different parameters on droplet size, particle temperature distribution and the gas permeability of the produced deposits. Unfortunately, also with this work no electrochemical tests could be performed or results published, yet, which would give the opportunity to evaluate thoroughly the state of the art and the potential for the relevant application.

As further information about thermal plasma processes particularly concerning the application of RF and induction plasma, as well and of other new methods also the study of further literature to be found in the references is recommended (Ref 31, 47-57).

5.3 Production of Anodes

Anode electrodes have to exhibit a number of characteristic properties to which first of all belong stability under reducing conditions, chemical compatibility, adapted CTE to the adjacent materials, high-electronic conductivity and a sufficiently high porosity for the access of the fuel, in most cases hydrogen or reformat of hydrocarbons, i.e., H₂ and CO, to the interface area between the electrode and electrolyte. Therefore, an efficient operation of an extended, well-structured three-phase interface of the gas phase with the electrolyte and electrode material is necessary. Porous Ni/YSZ cermets are the most frequently applied anode materials, at present, processed conventionally by wet powder and sintering methods. Recently also ScSZ (scandia stabilized zirconia) and other oxide materials find increased interest particularly for anodes of SOFCs at reduced operating temperatures (Ref 58).

One task of the oxide content within the anodes is to moderate the CTE-value to be more adapted to the value of the electrolyte. The Ni-content with the higher CTE is responsible for a good electronic conductivity. With standard Ni/YSZ anodes the volume shares of Ni, YSZ and pores are each about 1/3 where the porosity is mostly attained by starting with NiO which will be reduced by hydrogen in operation resulting in Ni with reduced volume on the one hand and an increased porosity on the other.

With Ni some drawbacks operating with technical reformat fuel have to be considered, e.g., catalytically enhanced carbon deposition, low sulfur tolerance, and redox problems when it is exposed alternately to reducing and oxidizing conditions reacting correspondingly with volume changes and eventually with disintegration of the anode cermet. A search is under way for replacing the Ni by a less problematic material. Another approach is to diminish the anode layer thickness as far as possible to cope better with these problems (Ref 34).

An extended work on the plasma spraying of Ni/YSZ anodes under reduced pressure was performed by Lang (Ref 59) with his PhD-thesis.

As with all plasma spraying experiments of mixtures of YSZ with Ni or NiO a strong influence of plasma power on layer density and as well as on the fractions of Ni and YSZ within the resulting deposit has been observed. Recently an article appeared about experiments with different types of powder feedstock in order to develop anode layers by atmospheric plasma spraying (Ref 60). The different feedstock comprised NiO or Ni powders mixed with YSZ as starting material, agglomerates of NiO and YSZ premixed on a sub-micrometer range, blended NiO/YSZ powder and of individual NiO and YSZ powders, separately injected. The performance of the produced APS anodes were subsequently investigated in single fuel cell tests. The results showed the importance for getting a large three-phase boundary that NiO and YSZ phases are homogeneously mixed on a sub-micrometer range. Under this condition almost all the compared procedures gave comparable electrochemical results. But, the anodes made by separate injection of NiO and YSZ into the plasma plume revealed a better thermal cycling behavior. With this type of anode, operated at 800 °C and H₂ as fuel, a power density of about 500 mW/cm² could be obtained according to this article.

An alternative way to make porous anodes is the use of Ni-coated graphite powder (Ni(C)) together with YSZ with the idea to get the porosity by burning-away the carbon content during and after the deposition process. Weckmann et al. (Ref 61) studied with a Triplex II system at the site of Sulzer Metco AG, Wohlen, Switzerland, the influence of the parameters on microstructure, porosity, roughness, triple phase boundary and electrochemical behavior of the products. As expected, using a fine Ni-graphite powder fraction (Ni(C)) denser layers with smoother surfaces and a higher share of YSZ within the layer were obtained with increasing the torch power.

In 2006 results of further relevant investigations could be added. NiO and Ni-coated graphite powders were sprayed with Triplex II in atmosphere and with F4 at reduced pressure condition. Fuel cells equipped with the Ni-graphite/YSZ (Triplex II) anodes showed better electrochemical performance and a higher-gas permeability than cells sprayed with NiO/YSZ and F4 under soft vacuum conditions, but, the degradation was higher with the first type of production (Ref 62).

Also LPPS showed some advantageous properties for spraying of anodes (Ref 43). Refke et al. used the LPPS equipment for processing of mixtures of Ni(C) with YSZ and reached the desired layer porosity of about 30% with a deposition efficiency of 40-50%. Also in the case of LPPS a specific adjustment of the spray parameters was necessary because of the different melting and deposition behavior of both powder components.

Considering the structure of an optimum Ni/YSZ anode it should, according to present knowledge, look as principally shown in Fig. 12 with the gradation of composition and porosity, where pore and particle sizes diminish together with the Ni-content toward the

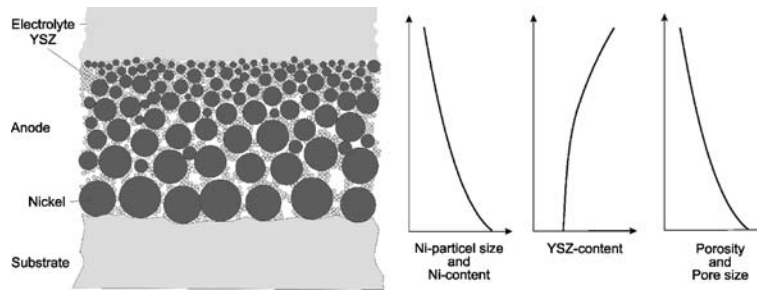


Fig. 12 Principle of a graded SOFC-anode

electrolyte interface. Plasma deposition methods show a high potential for producing such structures for improved anodes. More work in this direction should be done in future to take further advantage of this potential.

5.4 Thermal Spray of Cathodes

At the interface area of cathode and electrolyte the incoming oxygen molecules of the air are dissociated and the resulting oxygen atoms, by taking over of two electrons each reduced to oxygen-ions which migrate through the electrolyte to the anode side. Therefore, the electrolyte material should show besides a high electronic and ionic conductivity, a sufficient thermal and chemical stability and compatibility with the adjacent components at the high-operating temperatures, and in particular a high-catalytic activity and a well-developed structure to allow a good access of the air to the reaction zone. This reaction area, the three-phase boundary (TPB) at the interface between electrode and electrolyte, should show an extended and finely structured surface for advantageous conditions for dissociation and reduction of the oxygen and the transfer of the ions into the electrolyte bulk. In order to improve and extend this reaction zone a graded material and porosity transition from the electrolyte to the cathode side is advantageous.

Strontium-doped lanthanum manganite (LSM) with a perovskite structure is one of the materials suited as cathode material. At the operating temperatures it is a mixed conductor, i.e., conductive for electrons and oxygen-ions. The addition of oxygen-ion conductive electrolyte material like YSZ or CGO (cerium-gadolinium-oxide) particularly for the TPB-area can improve the cathode performance (Ref 63, 64).

Conventionally, the cathode material is put on the electrolyte surface with wet powder processing as a paste, where after drying the solid component has to be sintered to get a good bonding link between electrolyte and the interconnect. Thermal plasma processes that have a high suitability to make controlled graded layers are confronted with the problem that most perovskites are thermally sensitive, e.g., LSM can lose manganese or manganese oxide with the result that the perovskite decomposes losing its good conductivity and electrochemical activity.

Malléner et al. (Ref 24) were among the first doing plasma spraying of perovskite cathode material for SOFCs

and reporting about problems with decomposition. In this respect progress could be reported with the use of supersonic plasma jets for plasma spraying of such materials at VPS conditions. It turned out that in the short time of much less than 1 ms the decomposition can be kept below a critical level. For further depressing of the decomposition also powder feeding with oxygen can be helpful (Ref 27).

Nie et al. reported that the performance of plasma sprayed LSM cathodes for SOFCs can be improved with respect to conductivity and cathode overpotential by heat treatment in air at 1000 °C (Ref 65). Perhaps this was partially due to the restructuring of the perovskite phase.

A step further with cathode quality improvement was done by Barthel et al. (Ref 64). They compared the two methods VPS and FS (Flame Spraying) for production of porous composite graded, non-graded and bilayered cathode coatings containing $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$ (LSM) and $\text{ZrO}_2/12\% \text{Y}_2\text{O}_3$ (YSZ). The electrochemical performance of the cathodes, evaluated by impedance spectroscopy, indicated significant improvements. Also flame spraying as a new processing tool seems to have a good potential for future applications, according to this paper (Ref 64). Unfortunately, this work was not continued.

Kang et al. (Ref 66) applied an atmospheric pressure, reactive DC plasma spray system to deposit porous complex oxide films for potential application in planar SOFCs starting with a mixture of La_2O_3 , SrCO_3 , and MnCO_3 . Layers of coated LSM made from the mixture were compared to ones generated using a prereacted LSMO powder made by solid-state reaction. The results showed that the reactive-spray formed coating layer was superior to the coating layer from the prereacted LSMO powder.

With the goal of cost reduction a lot of work has been done with atmospheric plasma spraying using DC-torches and perovskite suspensions. First of all the process had to be developed to get stable suspensions and to inject properly into the plasma. Monterrubio et al. (Ref 67-69) worked first with attrition milled LaMnO_3 powder of mean particle size of 0.8 μm . It had to be realized that the plasma forming gas has a drastic influence on the obtained phases. As expected, hydrogen in the plasma forming gas has a too high heat transfer coefficient leading to decomposition. Ar/He and pure Ar are more suitable. Eventually, with limited heat transfer from the plasma and with a stable suspension containing a 10 mol% MnO_2 doped perovskite powder with 3 μm particle size best

results could be obtained concerning perovskite stoichiometry in the deposit.

In the whole suspension work, cited above, up to now, no electrochemical evaluation of the obtained products in SOFC configuration was performed or has been published. But relevant electrochemical results of experiments with suspensions can be found at Chen et al. (Ref 50). This article describes an approach for an integrated manufacturing process for SOFCs using a laboratory type plasma source called Triple Torch, where plasma jets of three independent plasma torches coalesce together within a chamber of controlled atmosphere. The three vertically arranged torches are tilted toward a central axis in which the water cooled material feed tube is positioned in that manner that its tip is located above the point where the three plasma jets merge. With this arrangement NiO together with YSZ was sprayed to make a graded cermet anode, and fine YSZ to deposit the YSZ electrolyte layer. For the cathode a process was developed which can be named as Thermal Plasma CVD (TPCVD). This deposition technique combines the control over the deposit composition of conventional CVD techniques with the high deposition rate of thermal plasma processes. In order to get LSM cathodes the nitrates of Sr, La, and Mn were dissolved in distilled water. This liquid is transported by means of a peristaltic pump and atomized at the exit of the injection probe with atomizing gas. The resulting XRD of the TPCVD perovskite coating represented almost perfect $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$. The cells generated by this arrangement showed with hydrogen as fuel at a standard voltage of 0.7 V and an operating temperature of 900 °C power densities up to about 250 mW/cm².

Also a torch with three plasma sources and central injection was recently applied in air for preparation of

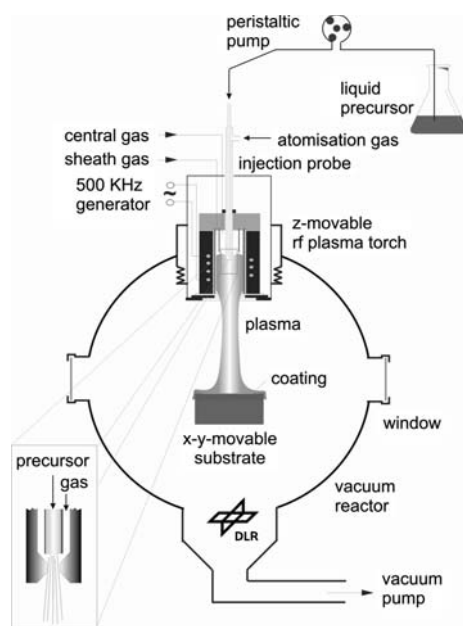


Fig. 13 Set up for RF-thermal plasma CVD (Ref 35)

porous SOFC LSM/YSZ composite cathodes, i.e., the “Axial III” of Northwest Mettech Corp., Richmond, British Columbia, Canada. LSM and YSZ powders were fed axially into the merged common plasma jet where argon and nitrogen was used as plasma generating gas to decrease processing costs and to avoid cathode material decomposition. Graphite pore former was added to the powder mixture in order to achieve sufficiently high layer porosity. The substrate was a tape-cast YSZ electrolyte. According to the article the production procedure appeared promising for the rapid manufacturing of SOFC electrodes, but the electrochemical cell performance was low explained by the considerable thickness of the tape-cast electrolyte (Ref 70) on which the cathode material was sprayed.

Toward the end of the 1990s induction plasma technology (RF-ICP) met rapidly increasing interest. Therefore, also synthesis and deposition of perovskite-type materials were considered. The paper of Schiller et al. (Ref 71) describes a new method for preparing and deposition of LaMnO_3 by reactive suspension plasma spraying using inductively (RF) coupled plasma with an oxygen plasma sheath gas. This process type can be characterized also as Thermal Plasma Chemical Vapor Deposition (TPCVD). Suitable precursor mixtures had to be developed, and best results were achieved by spraying a suspension of fine MnO_2 powder in a saturated ethanol solution of LaCl_3 with a 1 to 1 molar ratio of lanthanum and manganese. As-sprayed coatings and collected powder showed perovskite contents of 70-90%. After a posttreatment with an 80% oxygen plasma an almost pure LaMnO_3 deposit was achieved in the center of the incident plasma jet. For such tasks an assembly has been used corresponding to the principle shown in Fig. 13.

In the meantime a lot more work was performed on the use of induction plasma technology for synthesis of perovskite materials. Three examples of papers will be cited because of their SOFC relevance: the papers by Bouchard et al. (Ref 72), by Müller et al. (Ref 57), and by Schiller et al. (Ref 73): The first article describes the work with aqueous solutions of La, Sr, and Mn (Fe or Co) nitrates to synthesize almost stoichiometric submicron powders of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$. The papers of Müller and Schiller give overviews over plasma chemical synthesis of different perovskites.

With synthesis and in particular with the deposition of such complex oxides the thermal conditions have to be carefully controlled in order to avoid a decomposition which is particularly a problem with Mn-oxide containing species due to its high-vapor pressure. But, with adapted conditions attractive perovskite microstructures can be produced with TPCVD and heterogeneous nucleation. These structures promise due to the columnar crystals and the spaces between a highly extended surface for oxygen reduction and oxygen-ion entrance (Fig. 14). In the next step this process shall be used to deposit such materials as structured interfaces between SOFC electrolytes and cathodes.

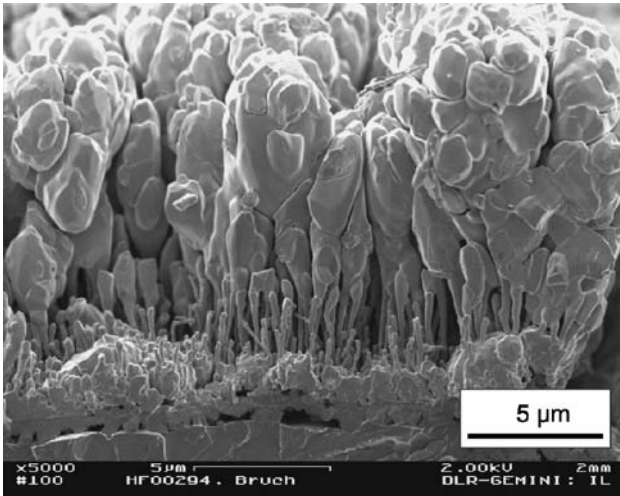


Fig. 14 Porous cathode layers by TPCVD (Ref 35, 57)

5.5 Thermal Spray Production of Interconnects

5.5.1 Thermal Spray Production of Interconnects for Tubular Cells. The main task of interconnects is to connect electrically in series the cells to get a suitable voltage within a stack. In the case of the tubular cells of Siemens Power Gen., where the substrates are the ceramic cathodes of perovskite-type material the interconnects are shaped as small strips along the tubes (Fig. 8). They connect electrically between the cathodes and the anodes of neighboring cells. Specifically composed LaSr-chromite is applied with APS, needing some postannealing (Ref 18).

Garcia et al. (Ref 74) compared for this task two different thermal spray techniques, i.e., High Velocity Oxy-Fuel (HVOF) using a modified nozzle and APS to process $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$ (LSC). The result was that with HVOF some of the LSC decomposed to non-perovskite LaCrO_3 which led to an increased electrical resistance. The paper reports that by heat treatment at 850 °C the perovskite phase can be recovered. In the case of APS the electrical resistance was lower, but a certain amount of non-melted and not-well integrated LSC and La_2O_3 was also within the layer to be found. As conclusion, further relevant work has to look for means to keep the thermal load during the process at a lower level, in particular the use of hydrogen as plasma forming gas and local overheating of substrate and generated layer has to be avoided.

5.5.2 Thermal Spray of Metallic Interconnects for Planar Cells. In the case of planar cells the interconnects have several tasks. Besides the electrical connection they have to care for the proper access of the reacting gases and for disposing of the reaction products (Fig. 2). Also they have to keep separate the different volumes of the reacting gases. Therefore, the interconnect material is exposed to reducing and to oxidizing conditions, as well. In first cell versions and with SOFCs operating at very high temperatures the interconnect material consisted and consist preferably of electrically conducting oxides. In advanced planar cells operating at moderate temperatures (~800 °C and below) chromium-based alloys as well as

chromium-containing steels are preferred materials, e.g., the ODS (oxide-dispersive strengthened)-alloy Cr5Fe1 Y₂O₃ (Ref 75) and specifically developed steels (Ref 76, 77) e.g., CroFer 22.

In the paper of Megel et al. (Ref 78) results of experiments with different ferrite materials are reported testing the long-term stability in oxidizing atmosphere. The result was that at about 850 °C steels like ZMG232, CroFer22APU, and Plansee ITM14 are suited for an operating time of more than 6000 h as long as the components have a thickness of at least 0.5 mm.

At the beginning of planar SOFC development only the ODS-alloys were available which had to be processed to suitable parts. But, such alloys are usually very hard and it is not easy to make components with a desired shape with them as it is necessary for interconnects (bipolar plates) with gas channels for planar SOFCs. Therefore, there was a search how to make the processing easier. In this connection also the Induction Plasma Spraying was tested for this task. ODS powder was deposited on negatively shaped graphite substrates which were first coated with boron nitride to ease the separation afterwards to get free-standing parts. This approach appeared promising, but the product was very brittle which made a time consuming postannealing necessary (Ref 79).

In the meantime the processing of such materials with more conventional methods has been considerably improved. Therefore, the spray approach was no longer followed. P/M (Powder Metallurgy) ODS Cr-alloys and P/M ODS ferrite FeCr-alloys could be introduced as a viable technology besides the increased use of special ferrites, mentioned above, which can be rolled and stamped (Ref 80).

5.6 Thermal Spray of Cr-Evaporation Preventing Layers for Interconnects

The high chromium containing alloys are protected from corrosion by its chromia scale (Cr_2O_3) formed in the oxidizing atmosphere on the cathode side. Under these conditions where also a considerable water (steam) partial pressure exists (about 0.02 bar), volatile chromium-(VI) species can be formed with the scale material (Fig. 15 shows principally the phenomenon). These volatile species can be reduced to chromium-(III) oxides at the critical electrochemically active triple phase boundary between the cathode and the electrolyte generating an interlayer causing a severe degradation of cell performance (Ref 81).

One option to suppress this effect or at least to diminish it considerably is to apply a ceramic protective coating for chromium retention which has to be of sufficient electrical conductivity, stable bonding and of good compatibility with interconnect and cathode material, as well. Different materials were vacuum plasma sprayed onto ferrite samples (Ref 82-85). Thereby, in the case of VPS application best results concerning Cr-evaporation preventing was achieved with $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$, which was sprayed with the grain size fraction $-32+16\ \mu\text{m}$. Figure 16 shows a cross section of such a VPS-produced protective layer on a chromium part.

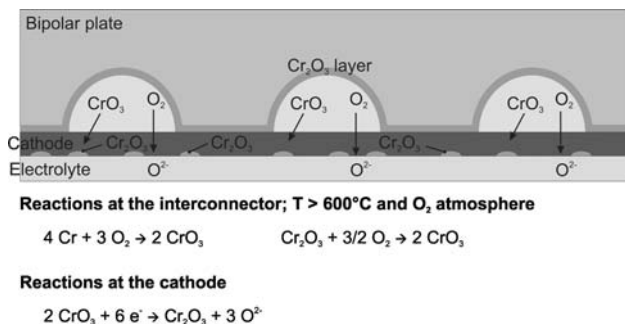


Fig. 15 Chromium problem with Cr-containing interconnects (Ref 81, 82)

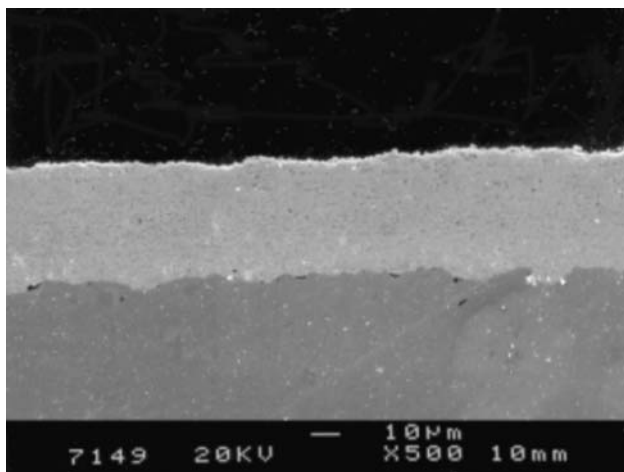


Fig. 16 SEM-micrograph of a VPS produced layer on a chromium part to limit Cr-evaporation

Besides LaSr-chromites also LaSr-manganites (LSM) were processed by plasma spraying with a F4MB torch (Ref 86). In this case of atmospheric processing of LSM powder a grain size of about $100 \mu\text{m}$ was used. But, to get sufficiently dense coatings a subsequent heat-treatment at 1000°C for 2 h was necessary. Also APS was applied to spray the spinels MnCo_2O_4 and $\text{MnCo}_{1.9}\text{Fe}_{0.1}\text{O}_4$ on Cro-Fer 22 APU which showed promising results (Ref 87).

Recently also the HVOF process was applied for first SOFC interconnect coatings, where LaSrCo-ferrite (LSCF) was processed to get hermetic layers (Ref 88). Unfortunately, no results of SOFC-relevant measurements are available.

5.7 Thermal Plasma Spray for Additive Components of Light-Weight APU-Cells

In section 3.2.3 already some information was given about SOFC-APUs (Auxiliary Power Units) for different assigned applications and also about the specific requirements to be met in order that SOFC-APUs become a success. The potential application fields cover electrical power for passenger cars, for trucks and busses, and also for electric vehicles as range extenders, for the maritime area, and the mine industry, etc., and even for aircraft. The

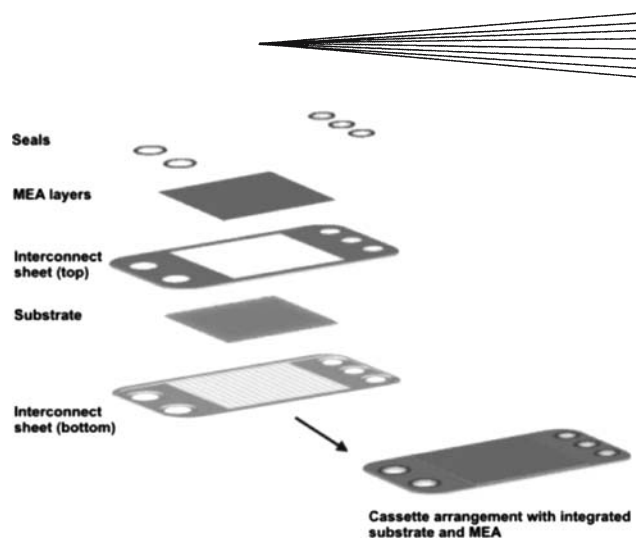


Fig. 17 Cell assembling of metal based APU cassette cells (Ref 35)

general demands to become competitive with presently used power generators are besides high specific power to volume and weight ratio, high fuel utilization, in particular suitability for relatively fast heating-up to operating temperatures, relatively long life time at frequent thermal cycles and, acceptable costs. This cost issue concerns both materials and production effort.

One approach to meet these requirements are very thin electrolytes or/and electrolyte materials with higher oxygen-ion conductivity, in order to allow the lowering of the operating temperatures which would reduce the degradation effects and hence increase the lifetime, shorten the start-up time and also open the usability of cheaper materials for several cell and system components. Thin Ni/YSZ anodes will also be less sensitive for redox cycles with hydrocarbon reformat as fuel. In this case relatively cheap but specifically adapted ferrite steels become suitable for operating temperatures up to about 800°C .

A German consortium under participation of the car manufacturer BMW has been very active in the field of SOFC-APUs with metal-based cells. Figure 6 shows one of the first versions of cassette-type cells produced by this consortium where the active part, the SOFC, is inserted in a recess of the upper shell by welding or other method. The cassette is formed by two shells which are welded together at the rims and also at the entrance openings for fuel gas and air. Figure 17 shows principally the cell components (Ref 35), where the way of assembling was already depicted in Fig. 7.

Ferrite materials, as described above, are used for the cassette sheets which are shaped by stamping. Hence, the surface of the sheets at the cathode (air) side has to be coated, as also already discussed above, to prevent Cr-release and poisoning of the electrolyte/cathode interface.

Porous ferrite parts, fixed to the lower cassette sheet, serve as gas distributing substrates on which the anode, the electrolyte and the cathode are successively sprayed in such a cell design suited for an entire production by thermal plasma processes. One example is given in Fig. 18 by the cross section of a cell with plasma sprayed anode, electrolyte, and cathode on a porous metal substrate.

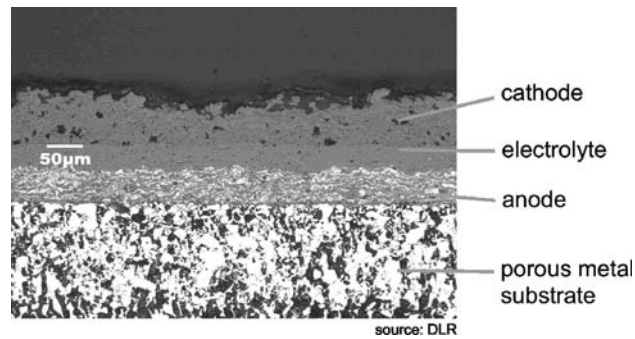


Fig. 18 Micrograph of a cross section of an entirely on a porous metal substrate plasma sprayed cell of DLR, early version (Ref 89)

But, with this design very early some new problems were encountered. One problem represents the required planarity of the components before and after cell deposition, because the electrolyte and the other parts of the cells have a very low tolerance against deformation. Therefore, the stresses due to rolling and stamping of the ferrite sheets of the cassette parts should be diminished as far as possible, e.g., by thermal processing. Another problem arises due to the material interaction of the anodes with the substrates. With standard Ni/YSZ anodes a fast mutual interdiffusion of the Ni of the anode and of Fe and Cr of the substrate will take place at operation. New, less conducting and less stable phases appear. Also the Ni changes the substrate ferrite into an austenitic alloy with a considerably increased CTE (Ref 84, 85). In Fig. 19 the problem of material interdiffusion between anode and ferrite substrate is demonstrated by means of an EDX-map. In order to prevent this detrimental effect on the anode side diffusion barriers have to be developed. An encouraging success was obtained with thin VPS-applied layers of doped LaCrO_3 (Ref 84, 85).

Starting with a very simple principle (see Fig. 2) of a SOFC with anode, electrolyte, cathode, and interconnect detailed work led to the conclusion that some additive layers are necessary to build a technically working cell. These additive layers are a field where plasma spraying can show its extraordinary qualities and where other methods can hardly compete. Figure 20 shows the schematic of the resulting multilayer design for APUs with ferrite metal substrates, as it is at present the base for further cell development (Ref 85).

With the progress of SOFC cell development and status a further problem appeared which concerns the arrangement of several cells to a stack. The cells have to be fixed together and at the same time the cell frames of the cassettes electrically separated from each other. This needs something between the cell frames meeting several requirements, e.g., geometrical fixation, sealing the gas volume and electrical insulation, all at about 800 °C. In this connection it has to be taken into consideration that with usual insulating materials like metal oxides the electrical resistance diminishes at least by three orders of magnitude when heated-up from RT to 800 °C. Therefore, the “cold-value” should exceed more than 1 MΩ to keep parasitic current losses at operation negligibly low.

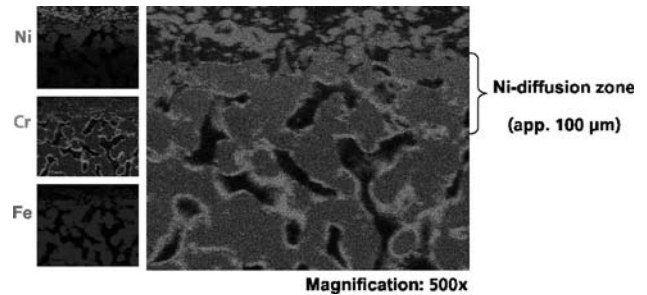


Fig. 19 EDX-map of substrate-anode interface after 550 h of cell operation at 800 °C (Ref 85)

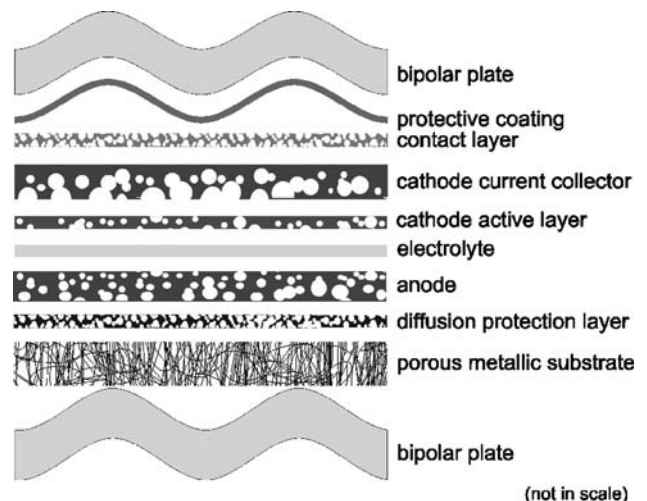
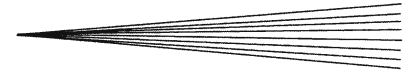


Fig. 20 Scheme of a DLR multilayer cell for metal based SOFC-APUs (Ref 85)

In several approaches special glass types were used as seals, but, it turned out that they need very soft thermal cycling conditions to survive several cycles.

Huang et al. (Ref 90) proposed an integrated composite seal using glass for sealing of SOFCs. The composite seal consists of a thin bond-coat of Ni-4.5wt%Al sprayed with APS directly on the Fe-Cr substrates of the cell housing. On this bond coat a thicker porous layer is



applied also by APS of alumina blended with stabilized zirconia. A glass filler is positioned between the two-coated parts and by pressure and temperature an infiltration of the glass into the porous layers takes place for sealing and bonding of the two parts.

In other approaches insulating layers of doped zirconia or Mg-Spinel were plasma sprayed on one of the two ferrite sheets of a cell and bonded to the next cell by a braze which contains a reactive component like titanium to get a fixed bonding with the oxide layer by generating oxygen bridges due to partial reduction of the surface oxides of the insulator. Very soon it turned out that the ceramic layers are very often not dense enough to prevent a penetration of braze material into them causing an electrical short circuit or at least a considerable reduction of the resistance. This problem seems to be solvable by double-layered insulating layers (Ref 91).

6. Integrated Cell Production by Thermal Plasma Technology

In the proceeding chapters mainly single components of SOFCs made by thermal plasma spraying were described. Only a very few papers can be found in literature where the production of entire cells is treated. In most relevant papers either APS or VPS has been applied. In some few cases different and differently adapted thermal plasma processes were combined.

Considering the suitability of the different technical approaches and methods and their technical maturity it has to be considered if their potential is high enough to become with further development a suitable method for mass production. In this connection, it is difficult to use the reported performance values as a means for a judgment, because for this purpose the geometries of the specimen and the test parameters, e.g., operating temperature, fuel composition, and fuel utilization rate, etc. should be comparable.

According to literature study almost forty years ago Tannenberger and Schmitt (Ref 20) started with the use of thermal spraying to make complete cells. Then, Spacil and Tedmo (Ref 92) were active by spraying the cell parts on an aluminum mandrel with a subsequent leaching of the mandrel with KOH followed by sintering of the resulting free standing product.

In the beginning of the 1990s several groups mainly in Europe and in Japan started with SOFC R + D by thermal plasma spraying, mainly with VPS (Ref 22, 24, 93). The obtained power densities, at these times, were still below 100 mW/cm^2 at an operating temperature of about 1000°C . The problem of thermal decomposition of perovskite material was already observed and parameters to suppress this effect were developed. For these experiments different types of substrates were used, e.g., porous sintered Ca-stabilized ZrO_2 on which the cathode was deposited or sintered porous $\text{ZrO}_2\text{-Ni}$ parts serving simultaneously as anode.

Few years later a considerable progress could be obtained with Ni-felt as substrates. Gruner and Tannenberger (Ref 23) reported a power density of about 160 mW/cm^2 at 0.7 V with VPS produced cells of 4.5 cm^2 at 910°C fuelled with $\text{H}_2 + 3\% \text{ H}_2\text{O}$. They claimed the production of the entire cell in a consecutive spray process (Ref 20). But, concerning the use of Ni-felt as porous substrates—Ni has attractive electrochemical properties—it turned out that for larger cell sizes the CTE (Coefficient of Thermal Expansion) of Ni is too high to be tolerable for the electrolyte. Cracks and also problems at redox-cycles appeared. Therefore, later on porous ferrite substrates replaced the Ni-felts, having the better CTE-adaptation but, unfortunately a lower-electrochemical activity together with a higher-electrical resistance. Also the upper operating temperature limit is lower.

Generalizing, it can be stated, that in the following years and up to now the application of plasma spraying for SOFCs has been and will be directed to two different geometries: on tubular geometries with ceramic substrates and on planar with metal substrates, the latter in particular for APUs.

6.1 Tubular SOFCs

The development of SOFCs with tubular or long monolithic “planar” (hollow) cells has been mostly intended for stationary applications. In the 1990s a strong relevant activity started predominantly in Japan, e.g., with Mitsubishi Heavy Industry or in USA with Westinghouse. With ceramic substrates not only VPS was considered but with increasing tendency also APS taking advantage from the potential of ceramic substrates to allow for postdensification of the electrolyte by sintering.

Okumura et al. (Ref 94) reported about the combination of APS and postsintering in the temperature range of $1000\text{-}1550^\circ\text{C}$ (3 h in air), using porous La-manganite substrates and for the electrolytes ZrO_2 with MnO_2 -addition to reduce the sintering temperature. Power densities of about 0.6 W/cm^2 at 0.7 V and 1000°C operating temperature could be obtained for a single cell, according to this paper.

An interesting technical approach with tubular geometry was pursued by Mitsubishi Heavy Industries in the 1990s where on support tubes of Ca-stabilized zirconia with a diameter of about 20 mm multiple ring-shaped cell structures were deposited, each comprising the fuel electrode, the electrolyte, and the air electrode. The electrodes of adjacent cells were connected by means of interconnecting coatings. VPS and APS were applied to make the electrolyte, where of course the VPS electrolytes showed considerable lower gas permeability. Under the test conditions (900°C) a current density of 200 mA/cm^2 was obtained, this meant 40 W per tube with 22 cells. Within this program also a pressurized ($\sim 5 \text{ bar}$) 10 kW class module comprising 414 of such tubes was successfully operated (Ref 9, 95). This approach was continued for some years with wet powder/sintering technology replacing plasma spraying.

One of the few activities, or better said the only activity where plasma technology for SOFCs reached already the level of considerable technical use represents the APS application of Siemens Power Generation Inc. (SPG) in Pittsburgh, PA, USA. There, the interconnects, the electrolytes, the anodes, and the anode interlayers are sprayed in atmosphere by DC plasma torches on the about 2 m long cathode tubes of ca. 2 cm of diameter. In the meantime the production increased from 100 to over 400 cells per month. According to the papers of Flower (Ref 18) and also of Huang (Ref 96) APS is a standard coating process for these layers and fully qualified as a mass manufacturing technology. APS replaced the former very expensive ECV process for making the electrolytes. But, with APS a postsintering, possible with such ceramic tube, is required to get the necessary leak-tightness.

Generators with such tubes are preferably assigned for stationary systems in the power range of about 100 to more than 1000 kW_e. With the recently installed systems efficiency values of almost 50% are obtained at a degradation rate of less than 0.2% within 1000 h and 900-1000 °C operating temperature.

As already mentioned above in order to increase the power density and to reduce the internal losses new cell geometries, e.g., High Power Density (HPD) and Delta tubes are under development to replace the “old” tubes with circular crosssection (Fig. 9) (Ref 18).

One of the key factors for a future success of the SPG SOFC technology will be the reduction of the final cost. One relevant approach is to enhance the power of the cathode-supported tubular SOFCs. Therefore, development work is under way to replace for example the presently used 8YSZ (yttria stabilized zirconia) for the electrolytes by 10ScSZ (scandia stabilized zirconia), which has a considerable higher oxygen-ion conductivity. In addition further work on materials concerns improved cathodes, interlayers at cathode and anode side of the electrolyte, and anodes, respectively. Bringing together the expected progress in geometry and materials a volume specific power density increase of almost 300% is expected according to the paper of Huang (Ref 96).

6.2 Planar SOFCs

As already mentioned above, first experiments with relatively small cells sprayed on planar substrates of Ni-sponges, felts or compressed nets showed interesting power densities (Ref 23, 25, 27, 97).

But, with larger geometries the thermal expansion mismatches between the Ni-substrate and the electrolyte and other layers caused problems. Therefore, further work toward the end of the 1990s concentrated on substrates with lower CTE, i.e., special types of stainless steels with high-corrosion stability (low-oxidation rate and stably bonded oxide scales). In particular ferrite steels and their processing and shaping attracted interest mainly for application in Auxiliary Power Units (APU) for cars (Ref 34, 35, 89, 98-102). Preferably DC-VPS has been applied to make the cell components. Recent efforts concentrated

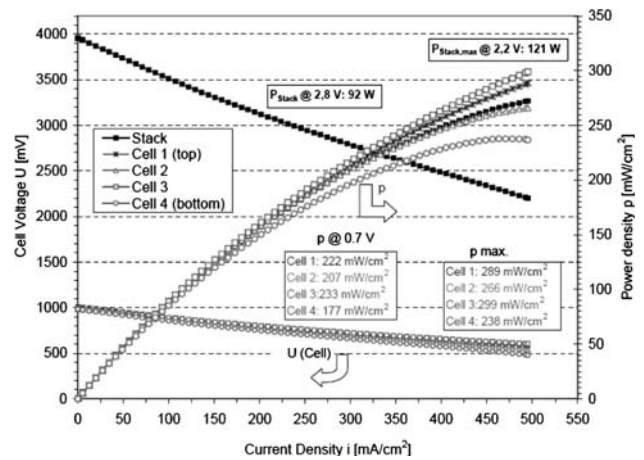


Fig. 21 Current-voltage and power density behavior of a short stack of 4 cells (125 cm² each) for mobile application, operated at 800 °C with H₂ and air (Ref 103)

on cells for reduced operating temperatures with ScSZ instead of YSZ for the electrolytes.

Some activity is also around using RF with the intention to combine either the in-situ synthesis of materials and their deposition (Ref 35, 64, 97), or also different plasma deposition methods into one consecutive process (Ref 49, 50, 52). In this connection also the work with LPPS with its attractive properties has to be mentioned (Ref 43).

State of the art with VPS produced cells of technical size with metal substrates can be characterized by a power density of about 250 mW/cm² in short stacks at 800 °C. Figure 21 shows as example the current voltage and power density behavior of a 4-cell stack with cells of 125 cm² for mobile application (Ref 103). At present, the not optimal density or inter-lamellar bonding of the sprayed electrolyte seems to limit the power density and to represent one of the main reasons of accelerated performance degradation.

For cost reasons also APS was qualified in parallel to VPS for this task, and a considerable progress could be made in last years (Ref 104). Ma et al. (Ref 105) reported in 2004 a power density of up to 150 mW/cm² at 800 °C. In this case the cell layers were APS sprayed beginning with the cathode side. Also heat treatment steps were included. Special attention was devoted to get dense LSGM (LaSrGaMgO₃) electrolytes (Ref 106).

In spring 2006 Hathamari et al. (Ref 107) reported already values of almost 0.5 W/cm² at 800 °C with APS-made SOFCs fuelled with H₂. As substrates served porous metallic tape-cast and sintered plates based on a ferritic Fe/Cr alloy. The progress was explained mainly by improved feedstock for the anode layers and their production. Very recently in November 2006, unfortunately without written paper and precise details, Renon (Ref 108) reported a power density of about 600 mW/cm² at 800 °C obtained for a (small) cell made by APS. According to this presentation 1 kW was obtained at this

temperature value with a planar APS cell of 2500 cm^2 , which means a power density of about 400 mW/cm^2 !

7. Production Aspects

In the following some aspects about industrialization and mass production of SOFC-units shall be described, shortly, mainly to hint on needs for further development work to meet the requirements successfully.

Concerning tubular cells, in general, plasma sources with higher deposition rate and deposition efficiency (DE) are important. Increased plasma jet and spray material velocity leading to electrolytes with improved density should be a means to reduce the required effort for postsintering to get the needed quality. Preheating of the tubular substrates would also show a better initial electrolyte quality with less stresses and higher DE. The replacement of the tubes by cells with a more flat geometry like with the new HPD and Delta configurations leads at least to a higher DE due to reduced overspray.

Concerning industrialization in particular planar cells for APUs with metal substrates are of high interest. As shown in Fig. 17 such cells consist of two ferrite steel sheets in which the active cell part, fixed on a porous ferrite substrates, is inserted in the top sheet. As layers with the potential to be produced by plasma deposition technology have to be considered:

- The diffusion preventing layer between ferrite substrate and anode
- The porous (graded) anode with the interface to the electrolyte
- The dense electrolyte
- The porous (graded) electrolyte/cathode interface
- The protecting layer for the interconnect (bipolar plate) on the cathode side
- And the dense and electrically insulating layer between the frames of adjacent cells to be brazed for geometrical fixation of the adjacent cassettes and for sealing the air volumes.

Relevant car manufacturer interested in the use of SOFC-APUs in passenger cars for an efficient electricity supply emphasize that in the first years at least 100,000 units with 3-5 kW_e should be produced per year to become relevant and to be on the learning curve leading to a necessary cost reduction in following years.

In the next part some evaluations shall show what this means concerning production rate, necessary resources and development goals for plasma sources, equipment, and installation.

100,000 APUs per year with 5 kW_e and 42 V mean at a cell voltage of 0.7 V and a power density of 0.5 W/cm^2 with 60 cells per unit a production rate of 6,000,000 cells per year, each cell with an active area of about 170 cm^2 . For 5 kW_e with this power density the whole active area of such an APU-unit amounts to 1 m^2 . Assuming in a rough

evaluation a maximum number of production hours of 6,000 per year then 1000 cells have to be produced per hour or about 17 per min, i.e., every 3-4 s one cell has to be finished. As a further assumption the three layers anode, electrolyte and cathode together with the interface layers should amount to a total thickness of about $100 \mu\text{m}$, which means that a volume of 1.7 cm^3 has to be deposited in about 4 s or about $0.4 \text{ cm}^3/\text{s}$. With a mean specific weight for the materials of 4 g/cm^3 1.6 g/s have to be deposited. At present the deposition efficiency for the materials under consideration scarcely surmounts 40%, therefore 4 g/s or 240 g/min have to be sprayed, which requires more than three advanced torches to get this spray rate.

In another view, a 5- kW_e -unit with 0.5 W/cm^2 of power density has in total an active area of about 1 m^2 . Under the assumption that the cell thickness amounts to $100 \mu\text{m}$ the whole volume of the cells is 100 cm^3 . With a density of 4 g/cm^3 and a DE of 40% the cell material to be sprayed for such an APU is 1 kg. 100,000 APUs mean therefore a material consumption for spraying of 100 t per year, where 60 t are overspray, which should be recycled as far as possible. A certain amount of the overspray represents the nickel for the anode which otherwise has to be dumped in a costly way as toxic waste.

Considering now the "plasma gas" consumption: with present standard plasma torches (F4, etc.) the powder throughput for SOFC materials is not more than 20-30 g/min with a "plasma gas" flow of about 50 standard liter per minute (slpm). About 1 kg of cell material needs therefore a processing time of 30-50 min, i.e., 1500-2500 standard-liter are involved, in a compressed state with 200 bar about 10 l. With a mean value of 2000 standard-liter or 2 m^3 for each of the 100,000 units 200,000 m^3 are consumed per year. Also this great volume could be economically interesting for recycling.

Going back with the consideration of the production rate where 240 g/min have to be fed through the torch(es): with the standard plasma sources, where 20-30 g/min are normal, about 10 of such torches have to work together to get the desired production rate. Advanced torches promise to be able to process about three times as much. This would reduce the number of torches to be involved considerably, under the precondition that the required product quality can be attained.

In a production line, where the different cell layers are consecutively made with specifically optimized plasma sources with optimized operating parameters, these sources have to work in series and each step should have equivalent production velocities and yields. With the experience that DE and quality is improved with increased substrate temperature the whole deposition process has to take place at constant high temperature in a series of reactors interconnected by interlocks. As in each reactor one specific material is sprayed recycling of overspray and "plasma gas" is also eased.

The production line begins with a vessel where the substrates are preheated to the deposition temperature and, without breaking of atmosphere and substrate temperature, respectively, the deposition process starts within

the next vessel, the anode chamber having an advanced plasma source with high throughput, going to the electrolyte chamber with several more or less standard torches in series for making the anode/electrolyte interface, the dense electrolyte (with high velocity plasma jets) and lastly for the electrolyte/cathode interface. In the next chamber the porous cathode conducting layer is formed, before, in a last chamber, the sprayed compound can cool down in a controlled manner.

To simplify the production process and the equipment and in order to keep the process velocity homogeneous the diffusion preventing layer on the porous ferrite substrate and the Cr-evaporation preventing layer as well on the cathode side of the interconnect should be sprayed separately. To cope with the desired production rate of 100,000 APUs per year at least three of such production lines have to be installed. As a consequence of this short evaluation the following topics for R+D and design activities are recommended:

- Plasma torches with higher stability, material throughput and deposition efficiency
- Development of automatically working control units for process and product quality
- Development of suitable equipment with interlocks, heated transport units, installations for overspray and plasma gas collection, stable and robust pumps coping with the process inherent dusty gases, etc.
- Research about recycling methods with cleaning and qualification of overspray and “plasma gas”, respectively.

8. Summary and Conclusions

In recent years considerable progress in thermal plasma diagnostic and in the knowledge concerning the interrelationship of applied parameters and resulting product quality could be made. Also a lot of different plasma spray methods have been developed and used to make SOFC components and also entire cells. Only few have already proven their potential for a reliable and efficient production of relevant layers and components and promised the status for a technical breakthrough for mass production where a continuous operation with high throughput and yield producing the desired quality is required. To these few examples belong the APS process applied by Siemens PG for making the electrolytes, anode interlayers, anodes, and interconnects of the tubular SOFCs. Concerning planar SOFCs it has to be stated, generally, that production methods based on wet powder processing and sintering steps show at present still a higher performance with power densities somewhere around 600 mW/cm^2 at $800 \text{ }^\circ\text{C}$ operating temperature and reformats of hydrocarbons as fuel, whereas for the relatively young spray methods the corresponding values surmount presently only about one half of the “sintering” value. Nevertheless, the plasma methods promise considerable advantages with

the potential to make relatively easily graded and efficient interface layers between the electrodes and the electrolytes and also to show advantages making the additional layers which are necessary for the metal based cells attracting now increasing interest for Auxiliary Power Units (APU) particularly for the electrical power supply for cars. Such layers are needed for preventing of the Cr-evaporation of the interconnect at the cathode side and for blocking the detrimental interdiffusion of anode Ni and Cr and Fe of the porous substrate. Also, the plasma processes allow for the production of very thin anodes which reduces the redox-problem, considerably. In addition, according to present experience, to come close to the values of sintered cells ways for further densification of the electrolyte and for a better crystallographic structure have to be found with adapted and improved plasma methods.

A critical review of published papers reveals that obviously work related to mass production is lacking. A considerable investment of tens of millions of € or \$ is necessary for a serious market entrance and for entering the learning curve which would promise a breakthrough success and the required cost reductions. In this respect concerning mass production as precondition for industrialization it has also to be evaluated whether production by batch processing or by continuous manufacturing of the different cell layers represents the more promising way.

Generally, in order to improve the cell production and the cell quality, and also to reduce the production cost, the following items are of highest priority, according to our opinion:

- Improved plasma sources with more power and more stability which generate plasma jets with a broader cross section and with reduced gradients of temperature and velocity across the jet dimension.
- Increased Deposition Efficiency (DE) and yield by more adapted powder fractions and proper injection parameters.
- Work on less costly materials, e.g., by evaluation of the required powder (precursor) qualities which potentially can in some cases be lower than with the presently used one.
- More work on combined synthesis and deposition of cell materials based on low-cost precursors where RF technology promises attractive advantages.
- Also, which is neglected at all up to now: aspects concerning the possibility of the recycling of “plasma gas” and of overspray have to be considered thoroughly.

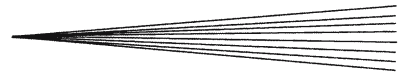
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