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Recent Developments in Metal Supported Solid Oxide Fuel Cells

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Abstract

Metal Supported Solid Oxide Fuel Cells (MSCs) offer certain very strategic advantages over the more conventional SOFCs, which comprise only ceramic materials. Since alloys such as Ferritic Steels are very similar in their coefficient of thermal expansion (CTE) with ceramic components, viz., Cerias, Zirconias, and Nickel Oxide doped with either of them, they could provide excellent thermal cyclability while maintaining a strong interlayer bond. Therefore, in an anode-supported cell the entire NiO-Ceramic support can be replaced by a ferritic steel porous support – the catalytically active NiO is therefore, a functional layer only. A huge savings in materials cost is achievable, since Cerias and

Zirconias (usually doped with Y, Gd, Sm rare earth elements) are considerably more expensive that ferritic steels. Lowering the capital costs for SOFCs is an extensive global undertaking with US DOE laying down targets such as ~$ 200/kW for the stack itself, in order for SOFCs to become competitive with grid power costs and to offer a power source that promises 24*7 power supply for critical applications. This will eventually lead to a premier electricity generation device in the distributed power space, with the highest known electrical efficiencies (>50%). Metal supported SOFCs need very robust, high precision and cost effective manufacturing techniques, which are scalable to high volumes. One of the main goals in this review is to show case some of the work done in this area since the last review (2010), and to assess the technology challenges, and new solutions that have emerged over the past few years.

Recent Developments in Metal Supported Solid Oxide Fuel Cells

Brief History of Solid Oxide Fuel Cells

Solid Oxide Fuel Cells (SOFCs) operating on fuels such as natural gas, have generated electrical efficiencies of over 50 % and with the promise of breaching the 60% barrier, at operating temperatures in the 800-850°C range, and in situations, where stack and system are operated with the ostensible goal of maximizing power output, without heat as a by-product. While efficiencies of SOFC systems operating on fuels such as natural gas tend to be lower in case of combined heat and power (CHP) output (relative to purely electrical power), SOFCs can still generate higher efficiencies than thermo-mechanical engines, and being modular, can be scaled up from less than 1 KW to 1 MW. The flexibility in sizing goes a long way in promoting SOFCs as a grid-independent and distributed power generator.

The original successful SOFC prototype was the well-known cathode supported system, developed by Siemens Westinghouse and reviewed by Singhal[1, 5]. The electrolyte used was 8 % Yttria Stabilized Zirconia (8-YSZ), with La, Ca-Manganite (LCaM) porous cathode support, and NiO-YSZ porous anode support, with operating temperatures in the regime of 900 to 1000° C. The La-chromate interconnect that was used in such cases was expensive. However, while many such cells were reported to deliver stable performances, the power densities were relatively low (< 0.30 W/cm^2), and, over the years, planar geometry has enabled cheaper materials for interconnects, shorter conduction paths for interconnects and lower operating temperatures (700-800^o C).

Planar geometries either work as electrolyte supported cells or as anode supported cells (ASCs). The former can operate effectively at temperatures of about 850^o C (in which case Scandium doped Zirconia (ScSZ) is preferred as electrolyte, due to its higher electrical conductivity relative to Yttria Stabilized Zirconia (YSZ); this is necessary, owing to the thick electrolyte [~200 micron and higher]). In the latter case (ASCs) temperatures can go lower, even up to 600^o C, depending upon the choice of the electrolyte (for YSZ electrolyte, temperatures of over 700^o C are practical, whereas for doped ceria electrolytes [Gadolinia Doped Ceria, GDC or Samaria Doped Ceria, SDC], 600^o C can be used, owing to the higher ionic conductivity, relative to YSZ).

Metal supported SOFCs (MSCs) – rationale, and their promise

The above-mentioned technologies are termed the 1st and 2nd generation SOFC technologies, which have taken the CAPEX costs as low as possible. While further reductions are slowly being achieved, albeit incrementally, DOE targets of about $225/kWe (Stack costs), $900/kWe (System costs) and 0.2 % /1000 hrs (System degradation) are still distant, and require drastic cost reductions. Even in the early years while anode supported cells with metallic interconnects were gaining ground in the SOFC community, the concept of using porous metal anode supports was being formulated, and has, over the past 10 years, reached technology readiness levels (TRLs) beyond 6, i.e., alfa to beta level testing in some cases, and almost 8 (product level) in case of Ceres Power.

The 3rd generation SOFC technologies, i.e., metal supported SOFCs (MSCs) are in effect, anode supported SOFCs but with an inexpensive ferritic steel porous anodic support (instead of the porous ceramic) of, although there are examples of metal supported cells with ferritic steels forming a backbone in the cathodic layers, as well.[6] The ability of the ferritic steel to bond with the ceramic

(YSZ, GDC, electrolyte or anode functional layer) and the similar coefficients of expansion (10-12 ppm/K) of the contiguous layers, makes it an excellent candidate for anode support. Ferritic steels are considerably inexpensive in comparison to either YSZ or GDC, and their usage promises a huge reduction in the materials cost. While there is considerable incentive to introduce MSCs, the complexities in the fabrication processes are very challenging, and need to be solved to ensure cell performance that is comparable with the anode supported SOFC.

The complexity in the fabrication of metal supported cells arises from the fact that multiple layers such as the anode support, the anode and the electrolyte must be sintered at much lower temperatures, as per the sintering requirements of the metal support. Some of the typical complexities during the evolution of a materials processing and co-sintering cycle for metal supported SOFCs include –

i. Sintering of porous metallic supports are limited by temperature, and cannot take place at the conventional ceramic sintering temperatures (1400 - 1500°C); in case of ferritic steels, temperatures higher than 1200°C enhance the possibility of Ni (from the contiguous anode functional layer) and Fe, Cr (from the support) counter-diffusion, and the approach towards the melting point of the alloy (1400-1500° C range is the melting region for SS430, SS446) As mentioned earlier by Tucker, over-densification[6] will result in the collapse of the pore structure and a drastic reduction in porosity, thereby causing major gas diffusional resistances in the anode.

ii. When starting with metallic powders, sintering operations should be carried out under reducing conditions or under vacuum to ensure that CrOx layers do not form on the surface of the support metal powders prior to the sintering temperatures. This leads to ‘constrained’ sintering, i.e., very poor adhesion between particles, and consequently poor strength[57]. However, in case of pre-sintered supports with a well formed pore structure, the electrolyte and anode functional layers have been sintered in air at temperatures of 1000°C (Ceres Power’s technology, which will be discussed further). The CrOx layers formed are electronically conducting and protect the metallic surface from any redox instability arising from flow interruptions of air leaks in the anode chamber. However, in such cases, the choice of the metal alloy is critical – it must have sufficient Cr to ensure stability in air – this was originally discussed by Tucker[6] and is further reinforced in this review, based on the recent advances.

iii. Porous Ferritic steel substrates prepared using fugitive pore formers (graphite, polystyrene, starch), by sintering in reducing conditions may result in carbon residues being left on the substrate, due to pyrolysis of pore-formers. To prevent this, pore formers need to be 'combusted' at lower temperatures in air, prior to the oxidation of Cr. To avoid CrOx formation, the switchback to reducing conditions should be done very precisely, and is definitely a non-trivial 2 stage operation.

iv. In a bid to reduce costs and enhance manufacturability, when colloidal methods (screen printing, inkjet printing) are used to deposit anode and electrolyte layers on top of the metal substrate, they too are constrained in their sintering temperature, which should not exceed the sintering temperature of the substrate. However, there are some rather interesting examples reviewed in this article wherein temperatures of about 1300° C have been used on metallic substrates.

v. Similarly, after the electrolyte is deposited by colloidal processes, densification of GDC / SDC/ YSZ/ ScSZ cannot be achieved at sintering temperatures of around 1200°C without the use of sintering aids. One can typically conceive of adjustments in particle size distribution in a bid to generate a highly dense green layer, which can then generate an impervious electrolyte upon sintering. This is a crucial process knowhow and very difficult to reproduce. Alternatively, sintering aids can be used to lower sintering temperatures[6], but that may lower electrical conductivity.

vi. Pre-sintered ferritic steel substrates will not undergo further shrinkage, whereas the deposited ceramic layers (particularly the dense phase electrolytes) will do so; therefore selecting the appropriate deposition process is mandated by the choice of the electrolyte as well[6], e.g., GDC can be deposited by colloidal techniques and sintered (and densified with the likely use of aids), whereas YSZ deposition by colloidal methods is usually co-sintered with green metallic substrates (under reducing conditions); alternatively YSZ and/or GDC can both be deposited on pre-sintered metallic supports by thermal spray techniques[6]. Nevertheless, the problem of electrolyte densification at much lower temperatures than for the all-ceramic cell, remains.

vii. On the cathode side – LSM, LSCF, require sufficient Oxygen during sintering, to retain their conductivity and structure. Hence, cathodes should be sintered in air, while the rest of the cell be kept in an air-free atmosphere. To avoid this problem, some groups have prepared a 2nd porous metallic cathode framework and infiltrated cathodic powder, and calcined the cathodes at temperatures much lower, relative the sintering temperature. A similar approach has been considered for the anode functional layer as well.

viii. The fact that the cell is structured on porous metallic substrates, requires more complexity in sealing operations, i.e., more than one sealing technique in comparison to conventional ceramic SOFCs.

ix. Metallic substrates (usually Ferritic Steels), tend to have Chromium levels of around 17-22 % by weight, but their stability in depleted fuel with high moisture levels (in regions of high fuel utilization in a stack) is suspect – which may necessitate coatings. This aspect was reviewed by Tucker[6] and has been implemented by a few system developers in this review as well.

None of these complexities are encountered in conventional ceramic SOFCs (ESCs and ASCs), since all layers in the latter can be sintered sequentially or co-sintered in air. The above summary only serves to describe the complexity of the manufacturing processes for MSCs – there are many solutions for these problems, and will be discussed in this review.

Further in this review, there will be a detailed description of MSC based stacks that have been fabricated by major groups/ companies, discussions on metal supports and their properties, variations in processes carried out by many groups, and their effects on cell performance, will be analysed. A wide range of literature, mostly in the 2010-16-time frame is reviewed, and the above complexities in metal supported and cell and stack fabrication are discussed.

REVIEW OF TECHNOLOGY AND PRODUCT DEVELOPMENT

Early review by Tucker (2010)[6] highlighting the work done by the Lawrence Berkeley group have discussed metal supports and their properties, multi-layer metal-ceramic co-sintering operations, their temperatures and how to introduce the cathode and anode electrocatalysts. The spin-off company from Lawrence Berkeley (LBNL) [7], Point Source Power also uses the LBNL metal support technology for its product.

Ceres Power, which was spun-off from Imperial College, UK, became the first company to effectively make a metal supported SOFC stack product[8-11]. Other major organizations who have been involved in the development of metal supported stacks, since have included –Topsoe Fuel Cells (TFC), which is no longer operational as an independent entity, Danish Technological University (DTU), Riso National Laboratory (Denmark), Forschungszentrum Julich (Fz-J) from Germany, Plansee (Austria), DLR (Germany), University of Toronto (as part of NRC's initiative on SOFCs) and several other groups in Europe and in other countries, e.g., universities in Korea and China have also been reviewed in this article.

Lawrence Berkeley National Laboratory (LBNL) and Point Source Power

LBNL has an extensive record of accomplishment for investigating metal supported cells (2000-10), reviewed extensively by Tucker[6].Their cell architecture was also made into a product, by a spin off company called Point Source Power (PSP). The PSP product called VOTO™ is operable in wood or charcoal burning stoves, wherein the fuel is stored biomass, with the temperature of operation in the range of 650-850° C[7]. The end use power is no more than a few watts, but is sufficient to charge mobile phones and LEDs for small flashlight or reading light applications.[7]

The idea of putting a biomass or coal in the anode in the cell is that it undergoes pyrolysis and partial oxidation when kept in the stove, generating syngas - the cell generates power from the decomposition of the solid fuel, and becomes a grid-independent charger. The 'fuel' is a 'card', with compressed coal powder/ biomass with binder, which can generate power for a while, enough to charge a Ni-metal hydride battery for powering a charger. Over time, it has the potential to scale up to domestic applications, using a green fuel source, viz., biomass   The usage of the metal supported cell technology enables a more rapid light-off than a similar ceramic cell[7].

Ferritic Stainless Steel (P434, procured from Ametek) is made via tape casting (with pore former, if necessary), followed by sintering in a reducing atmosphere at 1300^{o} C.[6, 7] A schematic of the cell architecture is shown in Figure 1, as also the device (Figure 2). In the LBNL/ PSP cell architecture, both cathodic and anode compartments have Ferritic stainless steel porous preforms. The cathodic and anodic electrocatalytic layers are 'infiltrated' into either compartment using their respective precursor salts/ salt solutions followed by calcination and reduction, at temperatures much lower than the sintering temperatures.

Cell and Stack Design of Ceres Power, UK[8-11]

The cell substrate is a ferritic stainless steel foil, perforated to create a gas permeable central region surrounded by an impermeable outer region (where there are no perforations). A thick-film cermet anode is deposited over the perforated region of the substrate and the deposition of the electrolyte occurs all around - over the anode and overlaps onto the surrounding steel, forming a seal around the edge of the anode. Ceres' design ensures that the porous anode is completely sealed by the non-porous electrolyte.

The electrolyte is complex in its architecture – it comprises 3 layers - one thick-film GDC layer ensuring gas-tightness, a thin-film YSZ layer to block electronic conductivity (due to the GDC), and a thin film GDC layer providing a buffer layer between the YSZ and the cathode.

The cathode too has a double layer - a conventional structure of a thin active layer where the oxygen reduction reaction occurs (close to the electrolyte) and a thicker bulk layer for current collection – this is a common cathodic architecture to optimize cathode performances in many SOFC designs.

The complexity in manufacturing processes that enable these ceramic layers to be deposited onto the steel substrate has been addressed in the following manner –

i. All major ceramic layers are deposited by screen printing, including the doped ceria electrolyte, giving a low cost, highly scalable cell manufacturing process.

ii. The cell is claimed to be fired in air rather than in a controlled atmosphere, at 1000^{o}C. It appears that the conditions for co-sintering are such that the substrate is relatively impervious to oxidation while sintering.

Another intriguing point relating to the cell-substrate co-sintering process is the low temperature of sintering – GDC does not undergo near 100 % densification till 1400^{o} C; it is probably a huge technological development to optimize the precursor powder material with the possible addition of sintering aids, that have resulted in a cost-effective simple co-firing technique, as described above.

Each repeating unit of a Ceres stack comprises the following –

i. The cell – Cathode (bi-Layer), Electrolyte (tri-layer) and the Anode (single layer)
ii. The substrate – unto which the cell has been co-sintered (ferritic stainless steel)
iii. A spacer - 'commodity grade steel'
iv. An interconnect plate – 'commodity grade steel'

Further intricacies are part of the evolution of the product design leading to an optimal architecture. Early performance data (Figure 3)[8] (2004) indicate over 300 mW/cm^{2} at 600 deg. C, for single cells, shown in the figure below. Over time, Ceres has made successful stacks with more advanced modifications, and is now producing power of about 10-15 kW that is being released to its customers[11].

In recent data (2015), Ceres power have indicated that the maximum power: weight ratio for their 'Steel Cell' is about 0.12 kW/ kg and shows degradation < 0.3 - 0.45 %/ khr for up to 6400 hours[11].

MSCs operating at 600^{o} C by Ceres may find applications in Auxiliary Power Units (APUs) for vehicles. APUs powered by SOFCs and particularly by MSCs, will lower off road emissions significantly. Currently, engine idling is carried out to provide essential facilities like refrigeration of consumable items, and for driving comfort – rest in rest-stops, etc. Operating SOFCs in APUs at 700-

800° C, are ideal from a fuel processing perspective, although, entire ceramic cells, as in a conventional SOFC stack, are not well suited for this purpose. MSCs offer the advantages of fast 'light-off', and can absorb shocks and vibrations much better than ceramic SOFCs, which makes them excellent candidates for vehicle APUs.

Overview of Stack and Systems development by German/ Austrian Consortium involving – DLR, Plansee, Elring Klinger AG, Sulzer Metco, BMW Group, Julich, KIT[12-15]

Prior to 2010, the German Aerospace Center (DLR) had introduced thermal spray processes for cell fabrication. The original cell was based on NiO + YSZ// YSZ //LSM and generated power density of 150 mW/cm² power density at 0.7 V at 800°C. Further collaboration of DLR with BMW Group resulted in performance improvements of 320 mW/cm² at the same temperatures. Plansee SE and Sulzer Metco AG with Elring Klinger AG, joined the original partners in targeting a proof-of-concept stack for auxiliary power unit applications (APU) [12]. The backbone for this cell was a porous ferritic steel of about 1 mm thickness, on to which were deposited all the catalytic and electrolytic layers by thermal spray/ plasma spray deposition methods.

A diffusion barrier layer (DBL) was also introduced between the steel support and the anode, - it was deposited by atmospheric plasma spray (APS) and in some cases, by physical vapor deposition (PVD). This DBL, comprising perovskite-type material (developed at DLR and Plansee) was used to prevent counter diffusion of Cr, Fe and Ni species from the substrate to the anode functional layer and vice versa – this innovation resulted in the enhanced durability of the cells beyond 2000 hours[12].

Plasma spraying has the advantages of short processing times and can be tailored for large scale production by automation, using robotics. However, attaining a desired microstructure, whether dense or porous, for the functional layers is significantly more difficult than achieved by conventional sintering routes. As per observations by the Plansee-DLR team, plasma sprayed electrolytes do exhibit gas leakage, which reduces the OCV, and is therefore the primary limiting manufacturing step in generating a high performing MSC.

In the schematic shown in figure 4 and the photograph in figure 5[12], ICs (Bipolar Plates/ Interconnects) were made from the Plansee ITM alloy, since it has higher mechanical strength compared to Crofer® 22 APU. A maximum power density of 0.6 W/cm² at 800°C with hydrogen + nitrogen is observed for this design.

The next step in the process involves GDC barrier layers, between the electrolyte and the cathode, deposited by EB-PVD (Electron Beam Physical Vapor Deposition). Impedance Data shows that with the barrier layer, ASR of the cathodes are lowered to 0.26 Ohm.cm^2, as compared to 0.57 Ohm.cm^2, without the barrier layer, when measured at OCV. While the detailed performance data is not mentioned in this work, the projected performance (based upon the lowering of the ASR of the cathode) is more than 1 W/cm^2 under the same conditions.

In order to make a stack with the above-mentioned cells, the strategy was different. A porous metal substrate of the size required was laser welded with 2 stamped plates (cassettes), as shown in figure 6. Plansee, with ElringKlinger AG, designed and fabricated the cassette-substrate assembly, wherein both components were made from a special Plansee ITM alloy – it is claimed that having higher strength, this alloy sheet metal fabricated cassette is thinner (0.3 mm, from the original 0.5 mm), enabling significant savings in weight which is desirable for quick light off (APU) applications[12]. The advantage of the 2 components being of the same media, i.e., ITM alloy, ensures that there is no 3rd component needed to join both, and laser welding would be an acceptable technique for the assembly. In this design, the cell-cassette assembly is separated from each other by insulation layers and air-brazes, to ensure hermeticity.

Prior to ‘assembling’ the cells on top of each other, functional layers are now deposited one by one, on this assembly as shown in Table 1[12]. Within Plasma Spray deposition two techniques, i.e., low pressure plasma spray (LPPS) and vacuum plasma spray (VPS), have been developed, in addition to the conventional APS. 2 stacks fabricated by LPPS and VPS each consisting of 10 cells, were successfully built and operated. The LPPS-based and VPS-based stacks exhibited stack power of about 160 W (current density of ~ 240 A/cm^2) and about 200 W (300 mA/cm^2), respectively, in hydrogen at a stack voltage of about 8 V (0.8 V per cell, for a 10-cell stack) (Figure 7).

Further development of the so-called ‘next generation’ metal supported cells, was carried out as part of the BMWi (German Federal Ministry of Economics and Technology) funded projects - MS-SOFC and NextGen MSC[13]. The Auxiliary Power Unit (APU) technology development (also classified as NextGen MSC), was led by AVL List GmbH to establish a reliable and affordable 3 kW SOFC APU system. The other members are - Plansee SE, Forschungszentrum Jülich and Karlsruhe Institute of Technology (KIT). This appears to be a collaboration between R & D institutions such as Julich and KIT providing scientific support, and from industrial commercialization partners such as Plansee and AVL List Gmbh (manufacturing of cells/ repeat units, systems development and integration, and stack testing).

The key elements of the NextGen MSC are as follows[13] –

i. Ferritic Fe-Cr alloy with 26% wt Cr (Plansee ITM alloy) as porous substrate of about 1 mm thickness; 2 sizes of substrates were used – one of them 7.5×7.5 cm^2 and the other, 13.8×13.8 cm^2.
ii. Diffusion barrier layer (DBL) deposited on the substrate to prevent Fe and Ni counter diffusion between the anode and the substrate.
iii. Ni-YSZ anode layer (25-50 micron) coated further on top of the DBL – it ‘fills’ the coarse porous morphology, covers it completely, so that the electrolyte can be ‘laid’ on top of it with minimal undulations.
iv. Sintering of anode carried out under reducing atmosphere at temperature greater than the operating temperature.
v. A dual layer electrolyte – slightly porous YSZ layer with GDC thin electrolyte layer, prepared by PVD (sputtering). The pore size of this adaptation layer is much smaller than the anode pore size, which makes it easy to coat it with dense phase GDC (CGO) with a thickness of 1-2 micron.

Hermeticity procedures (gas tightness of electrolyte) are described in detail[13]. From the existing half cells (cells without cathode), appropriate dimensions were cut for testing and for stack building (5×5 cm^2 and 10×10 cm^2).

LSCF ($La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$) cathodes were deposited via screen-printing on top of the leak-free cells. They were dried and sintered at about 1080° C for standard Anode Supported cells (which are used for comparison), but were left 'un-sintered' for the metal supported cell. The cell cross section is shown in Figure 8 – observe the very thin DBL and the electrolyte layers.

The single cell performances in the 675 to 823° C range are shown in Figure 9. At a voltage of 0.7 V at 823° C, current density of about 650 mA/cm^2 is reported, which corresponds to a power density of 455 mW/cm^2. A comparative analysis of the MSC performances with that of a standard anode supported ceramic cell (ASC) was also done – shown in Table 2.

The authors have specified that the comparisons have been made considering some of the differences in processing and pre-treatment which are different for MSC cell vis a vis Anode Supported Cells (ASC), viz., reduction temperatures for ASCs are 900° C compared to 850° C for MSCs; un-sintered cathodes for MSC vs 1080° C sintered cathodes for ASCs. The ASC tests were done in humidified Hydrogen, while those for the MSCs were at in dry Hydrogen/Ar mixture.

Despite the differences, it was also established that the 'leak rates' (lack of hermeticity) either from seals or from electrolytes, have not only the effect of lowering OCVs, but are also responsible in part, for the lower performances of the MSCs (Figure 10). Therefore, it is very clear that MSCs fabricated at the German Consortium, as also by other metal supported stack developers continue to face leakage; achieving leak free/ hermetic operation continues to be one of the biggest challenges for metal supported cell and stack technology[13].

The above-mentioned cell was part of the Gen A[14] class of cells. Further improvements are shown in the configuration called Gen B (Figure 11), wherein, the YSZ is no longer an 'adaptation' layer, but now becomes the electrolyte, and is only 3-4 micron in thickness. The CGO (GDC) 1-2-micron layer is now only a barrier layer.

Physical Vapor Deposition (PVD) was used to deposit the DBL layers and the electrolyte layers, particularly for Gen B cell, where the electrolyte is now 8-YSZ, is now decreased significantly in terms of thickness (CGO layer is now a barrier layer). The tested Gen B cell showed much higher current densities of 1.52 A/cm² at 0.7 V and 820°C, which translates to a power density of 1,064 mW/cm^2. However, the OCV is about 0.967 V, which indicates a relatively high gas leakage rate, and as seen in much of the developmental work, that appears to be one of the major problems, i.e., generate a consistent dense phase electrolyte using deposition techniques. Over a 300-hour period, very little degradation was observed as well[14, 60]. Shown below (Figure 12) is the manufacturing cycle for Gen B type cells[14].

The microstructure for a half cell (without the cathode) of Gen B is shown below in Figure 13.

From the system side, AVL List GmbH was coordinating the development of a 3 kW SOFC APU unit and testing it with the recirculated anode exhaust gas[15], under real operation conditions – Anode Exhaust recirculation is critical for use in APU, where moisture must be introduced entirely from the product stream. The NextGen MSC cell (Gen A and B) were used for the stack build. The product constraints are very challenging and severe as well, since commercial diesel has high sulfur levels (high enough to damage the fuel processor and the anode, in case of breakthrough), the system should be small with stack weight < 100 kg to ensure compliance; it was then successfullytested up to 3000 thermal cycles and up to 30 redox cycles.

During the APU testing, simulated Diesel Reformate gas - 50% N_2, 15% H_2, 14% CO, 11% H_2O, 10% CO_2 was used. At a fuel utilization of 80% a standard MSC can still achieve a cell performance of 200 mW/cm^2 at 0.7 V, at stack operating temperature of about 750 ^oC. The cell performance is a strong function of Fuel Utilization, as seen by a huge drop in power density from 630 mW/cm^2 to 200 mW/cm^2 as FU increased to 80% (Figure 14)

Further advances on the MSC cell (B type) have been done with respect to improved quality of cathodic materials, such as $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC), $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ (LSCF), and a mixture of LSC, LSCF with graphite. Graphite has been used for enhanced cathode adhesion to the electrolyte. Graphite oxidation is also reported to promote in-situ cathode activation, and has resulted in better cathodic performances[15]. Figure 15 highlights the various advanced formulations with improved cathodes and anodes – versions C, and D. Figure 15 shows very high current densities of over 1.5 A/cm^2 (> 1.05 W/cm^2), achieved with metal supported cells in Hydrogen feedstock at 850^o C, which upon commercialization may be a very cost effective product.

Development of MSCs stacks at Topsoe Fuel Cells and groups at DTU, Riso, Denmark (EU projects METSOFC, METSAPP and Danish funded)

This development encompasses novel cell and stack manufacturing processes including infiltrated nano-structured electrodes, Sc-doped zirconia electrolytes for operation in the temperature range 600-700^o C.

The cell fabrication in the METSOFC program, is carried out as follows[16-18] -

i. Tape casting is a very well-known highly scalable technique and is implementable not only on ceramic powders but also on metallic powders. Relatively thick metallic ‘tapes’ followed by thin electrolyte (Sc-YSZ, co-doping of Y and Sc on Zironia) co-tape casting was carried out, followed by drying and lamination, and then cutting into the right size, allowing for shrinkage during the sintering process.

ii. Co firing of a tape cast zirconia electrolyte and the powder metallic support (Ferritic Steel Fe–Cr-powder 22 % Cr-based stainless steel alloy [18]) - Co-sintering processes are proprietary, although the authors mention that it was carried out above 1000^o C in a Hydrogen/Argon atmosphere.

iii. Infiltration of the electrocatalyst precursor solutions followed by calcination at 350° C for 2 hours, resulted in a coating of nano-particles on the porous metallic surface – 10 wt % Ni on $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC20)[18].

iv. The barrier layer of $Ce_{0.9}\ Gd_{0.1}\ O_{2-\delta}$ was deposited on the cathode side of the electrolyte by reactive pulsed DC magnetron sputtering (PVD).

v. The cathode and cathode current collection layers were applied by screen-printing of $La_{0.58}\ Sr_{0.4}\ Co_{0.2}Fe_{0.8}O_{3-\delta}/\ Ce_{0.9}Gd_{0.1}O_{3-\delta}$, and $(La_{0.6}Sr_{0.4})_{0.99}\ CoO_{3-\delta}$, with the latter also acting as current collection layer. The layers were fired in situ during cell testing (Figure 16 shows microstructure of half-cell by Topsoe[18]).

The developers at Riso/ Topsoe/ DTU emphasize the advantages of metal supported cells in terms of their high ductility and robustness. Laser welding and brazing have also been used for joining and sealing. Metal supported cells of over 300 cm^2 have been manufactured at DTU, and cells with 12 x 12 cm^2 foot print have been tested for stack development around 2013[17].

A long-term test of 3000 hours was carried out on a metal supported cell at 650 °C, with H_2 (4 % H_2O) and a current of 0.25 A/cm^2, under very low fuel utilization. Very low degradation rates of 0.036 $\Omega\cdot cm^2$ and 0.9 % of the cell voltage per 1000 h were observed in the temperature regime of operation (Figure 19) – although the degradation rates increase with fuel utilization, reported in one such case – this is due to the corrosive effects of product moisture. The authors emphasize the issue of stability of the ferritic steel in the presence of high moisture contents, under high fuel utilizations in a stack. In a bid to overcome the corrosion of the anode support at high fuel utilizations, protective coatings offer one solution. Alternatively, Topsoe Consortium has expressed interest in using Nb-doped Sr TiO_3 anodes, which can withstand corrosion under high moisture levels in the anode. This is part of the METSAPP program, which is discussed further ahead.

Data from testing of TFC cells is shown below in Figures 17 and 18, demonstrating over 350 mW/cm^2 power density, at 0.7 V, in 5*5 cm^2 cells, as well as in button cells, at a temperature of 650° C. Fuel and air utilizations of less than 10% were maintained during the testing.

Other salient features for metal supported cells include[18] –

i. Metal supported cells show considerably stability for 1000 h at 650 °C than conventional Ni-based anode-supported cells, under 96% Hydrogen and 4% moisture feeds (about 4.5% voltage loss/ khr, at a constant current density of 250 mA/cm^2).
ii. Metal-supported cell design is shown to withstand 100 redox cycles, without any degradation or failure. The infiltrated Ni morphology is very effective in preventing redox instability despite agglomeration of Ni, partly because the loading is low and will not create stresses on the surrounding electrolyte phase. Redox cycling tolerance is critical in cases of disruption in fuel supply, and the ensuing leakages of air that cause Ni oxidation and volume expansion.

Further work on the METSOFC improved cell performances and lowered degradation from 4.5% to 0.9%[19]. This was followed by integration into stacks (144 cm^2 area cells) at the erstwhile Topsoe Fuel Cells. Stacks developed at Topsoe had 25 cells in them and their performances are discussed further.

The stack of 25 cells, delivered 450 W at 700°C at a voltage of 0.7 V per cell (Figure 18). The stack testing, over a period of 250 hours, shown in Figure 19 reveals a degradation rate of about 160 mΩ cm^2/khr. This is attributed to the cell oxidation failure mode (due to moisture levels), since the operating Hydrogen fuel utilization is about 60 % and the air utilization, around 40 %. It must borne in mind that due to infiltration of Ni, the loading of Ni is very small (about 0.3 wt% anode[18], hence it is therefore likely, that the Ni → NiO transformation could become a principal cause for degradation, particularly in case of small leaks via seals, or internally through electrolyte imperfections[18] in addition to the expected corrosion of metallic supports at high moisture levels.

In summary, MSCs developed, by the Riso/DTU/Topsoe[16-19], were scaled up in size from 4 to 144 cm^2, which was incorporated into a 25-cell stack, which has been shown to work effectively. The authors report ASR performance of the button cells to be less than 0.3 Ω.cm2 measured at 650 °C. However, tests with simulated diesel reformate gas (containing 0.65 ppm Sulfur) resulted in high degradation rates, which is a very different issue, altogether. From a cell perspective, ferritic steel corrosion in the presence of moisture/ fuel, could be one factor contributing to degradation, although it appears to be obfuscated by the high Ohmic resistance building up over time in the anode, due to possible Ni oxidation.

As a spin-off from METSOFC, a new EU FCH JU project METSAPP was launched in 2011[20A, 20B], aiming at further improvement in durability and lifetime for residential applications, viz., 650-700°C operation, for 20-60 kHrs, as well as mobile applications (APUs for example, 650-700°C operation, for 5-10 kHrs). The following targets were set[20A]

i. Robust metal-supported cell design, with ASR_{cell} < 0.5 Ohm.cm^2 at 650°C
ii. Scalable process for Cell manufacture
iii. Cell/ stack degradation rates < 0.25%/khr
iv. Stack ASR $_{stack}$ < 0.6 ohmcm^2, 650°C
v. Robustness of 1-3 kW stack verified – thermal and redox cycling, stability

The METSAPP project[20A, 20B] included the development of metal powder for supports, novel anode design, high performance cathodes, cell-stack assembly and integration, component level testing, and development of coatings for ferritic steel Interconnects (ICs) for high oxidation resistance and lowering Cr evaporation in air (Chromium poisoning).

The base case cell design of the METSAPP project is based on a multi-layered structure obtainable by cost effective ceramic processing techniques such as powder metal tape casting, lamination, co-sintering and infiltration. As observed in Figure 20, the cell design comprises a porous Fe-Cr (ferritic steel scaffold) into which GDC and Ni are infiltrated (after the other layers, viz., electrolyte, barrier layer and cathode are deposited, and co-sintered) in the end.

Other areas of development include – coatings for corrosion protection of the porous framework, new anodes ($SrTiO_3$), e.g., STN-FeCr designs.

Sheet Metal Interconnects (ICs) coated by PVD for prevention of Cr poisoning are being investigated. The cells/ stacks are targeted for operation till 650° C only, and therefore the emphasis is clearly on ferritic steel alloys that are commercially available, to reduce materials cost. Furthermore, the sealing of the IC and the cell by usage of techniques such as laser welding is conducive towards scale up and manufacture.

Efforts at Consortium comprising – CEA-LITEN, CNRS and Baikowski (France), Hoganas AB (Sweden), SOFC Power (Italy), SINTEF (Norway) and IKERLAN (Spain), funded by RAMSES EU project[21]

A significant effort in the form of the Ramses EU project is yet another consortium effort towards the development of materials, components, and processes, necessary for metal supported cells. The consortium members with their own technical areas of strength, contributed to this effort, e.g., Hoganas providing the metallic powders for the substrate, SINTEF providing La, Mn coating solutions for the metallic substrate to minimize corrosion, Baikowski with the 8-YSZ electrolyte power sinterable at 1200 °C. The project has addressed both planar and tubular cell geometries with their own advantages viz., Tubular gives better cyclability although Planar provides higher performance.

One of the principal goals in this project was to make ferritic alloy steels with doctored anti-corrosion properties. As part of the extensive work on making porous metallic supports, the group investigated a series of alloys containing Fe, Cr and optimized the compositions to ensure CTE match with the ceramic functional layers, and to ensure good Oxidation resistance (particularly from the steam/H_2 side, anode side). Ten different alloy compositions were tested – SS powder containing 22% Cr with a Si content < 0.15% wt was chosen as optimal material for the substrate. Anti-corrosion resistance was found to be excellent for these compositions as also CTE match with the contiguous ceramic layer.

Metal supports were used on the anode side (Anode side metal supported cells, AMSC) for both tubular and planar geometries, whereas Cathode Side metal supported cells (CMSC), which is very rare, was tried and tested for planar cells. To prevent oxidation in the air atmosphere, dip coating the porous metal support with protective coatings, such as La $(Mn_{0.5}Co_{0.5})_{0.8}$ and $LaMn_{0.8}$ was done and fast ‘curing’ carried out after each coating, at 900°C – steps of coating and fast curing done 5 times in total. Eventually these will develop into protective perovskite coatings and protect the cathode from Cr poisoning. The authors also claim that their alloy steel is stable to oxidation in air on the cathode side, even without coating, although the same coating on the anode side was necessary for resistance to steam-Hydrogen mixture (H_2-Steam-Ar mixtures, at 600°C was used to test), and was stable to degradation for over 500 hours. As per the requirement for the RAMSES project, the authors found that over 500 hours, an oxide scale of less than 3 microns has formed – this has been deemed satisfactory.

For planar cells, green sheets from metal powders were pre-sintered at 1100-1150°C with a 30-minute soaking period at this temperature. Porosity of 30-40 % was observed for the porous substrates generated herewith.

The Tubular cells prepared in this project were 50 mm long and 14 mm in diameter (like CROFER 22 APU tubes) on to which were deposited the diffusion barrier layer (Y-doped Ceria in this case), by dip-coating. The anode layer (NiO-YSZ) was next deposited, also by dip-coating, after which electrolyte layers were deposited by powder Spray methods. This half-cell was sintered in 10% hydrogen-Ar mixture between 1350 to 1370°C. The cathode (LSF-SDC composite) was then applied via dip coating, and fired in-situ up to 950°C – the cathode coarsened as the cell was being prepared for electrochemical activity – measured in the 600 to 800°C in a 3% H_2O/ H_2 mixture.

The main purpose of these kinds of coatings was to ensure that Ferritic steel support is protected from oxidation in air, either under air or in wet hydrogen (wherein high fuel utilization can be simulated) conditions. Power densities higher than 500 mW/cm^2 at operating voltages of about 0.7 V, at 800°C reported in Figure 21.

The consortium above has achieved the following[21] –

i. Metal substrate optimization, to meet targets for low cost, sintered in low oxidizing atmosphere and with resistance to Oxygen

ii. Preparation of customized electrolyte powders (ScSZ) to achieve sintering at temperatures lower than 1200^{o} C, for conventional 8-YSZ

iii. Polarization values of about 0.37 Ω.cm^2 at 600 ^{o}C were observed for a Ni-8YSZ anodes, and 0.2 Ω.cm^2 for the Nickelate anode for a planar geometry cell.

iv. ASRs of about 1.56 Ω.cm^2 were observed for the overall cell at 600 ^{o}C and about 0.42 Ω.cm^2 at 700^{o}C

v. Cyclability data on tubular cells also shows a robust performance over 500 thermal cycles, i.e., no change in voltage over a 2900-hour period, and constant ASRs reported over the test period.

Metal substrate optimization, to meet targets for low cost, sintered in low oxidizing atmosphere and with resistance to Oxygen.

University of Toronto

The group at Toronto has its strengths in atmospheric plasma spray techniques. The work done primarily is at the Centre for Advanced Coating Technologies (CACT), at the University campus itself. For metal supported cells, the promise of significant savings from substitution of ceramic with ferritic steel could be nearly offset by the complexity in manufacturing – hence, it is vital to seek out cost effective methods for production of cells and stacks. Atmospheric Plasma Spray can be readily automated and scaled up for large areas and for higher production volumes. There is no sintering furnace requirement, since the densification is carried out during the deposition, itself.

Metal supported SOFC cells have demonstrated power densities of around 700 mW/cm^2, at 750 ^{o}C. Kesler et al.[23] highlight very clearly the importance of preparing fully dense coatings of electrolyte layers on top of the porous metal support. The microstructures obtained below are after a series of plasma spray depositions.

The SEM micrographs (Figure 22) show 2 substrates being used – one, is a commercial SS430 sample, and the other one, prepared from powder metallurgy, using powders (21-23% Wt Cr), and pelletized to 1 cm diameter, and sintered in Hydrogen (with PVB binder and PMMA pore-former).

The in-house prepared porous substrate has much higher porosity and smaller pore sizes. Standard techniques to protect stainless steel substrates such as dip coating were followed here too, wherein La and Y- Nitrate solutions were used for dip-coating onto the substrate – after heat treatment they would form La or Y Oxides, as a protective layer against corrosion. A similar technique was followed in the Ramses project as well.

Plasma Spray deposition of the layers of the fuel cell was carried out in a sequence –

1. Anode layer being deposited first on the metal supports, and reduction in Hydrogen, followed by
2. Deposition of the electrolyte
3. Deposition of the cathode

The depositions were accomplished by Hydrogen-Argon plasma (5% H_2-Ar) using torch arc currents ranging from 450 to 750 Amp. Substrates were preheated prior to deposition by plasma itself prior to deposition. Plasma Spray of aqueous suspensions of YSZ powers was achieved as well – wherein, the liquid phase comprised water, ethylene glycol and ethanol[23]. Powder suspension (APS), were used for electrolyte deposition, and were optimized over time (Figure 23, Left), in a bid to lower the imperfections, and cracks that appeared due to high thermal gradients during deposition, and the fast cooling that accompanies the stoppage of plasma – the technology and science behind Plasma Spray is discussed further in the article. Kesler et al.[23] have improved the OCVs from 0.92 V to 1.08 V at 750^{o}C over a one year period as shown in Figure 23 (left). The best performances of the cells with the highest OCVs, are about 300 mW/cm^2 (Figure 23, Right).

The authors have specifically used SDC and LSCF cathode powder and deposited it over the electrolyte using Powder plasma spray (PPS) – the powder used is dry in contrast to suspension of powder in liquid phase for the electrolyte, as mentioned earlier. Modifications and variations in cathode powder depositions have been tested as symmetric cells, and were about 0.101 Ω.cm^2 and as low as 0.082 Ω.cm^2 depending upon how the LSCF and SDC powders were mixed.

NiO and YSZ compositions for anodes, as well as Cu-SDC, Cu-Co-Ni-SDC – were prepared by three plasma routes – suspension powder (SPS), powder suspensions (APS) and usage of precursor solutions (SPPS). In the last method, the synthesis of the mixed oxide occurs simultaneously as the deposition[23]. The overall performances of the cells are about 400 mW/cm^2 at 0.7 Volt (Figure 24), without much difference between the SPS, SPPS, and the APS.

REVIEW OF METALLIC POROUS SUBSTRATES AND INTERCONNECTS (ICs)

Most ferritic steels (SS430, AISI441, Crofer APU) while differing in the quantity of chromium in the alloy, have CTEs of about 10-12 ppm/K which are compatible with ceramic layers like YSZ and GDC. Ferritic steels are also very inexpensive as listed in Table 3, (reproduced from Tucker's review) [6] [400-series (Ferritic) steels are about $2/kg (2009), in comparison to Ni, which is $18/kg, and NiCrAlY ($63/kg)]. These numbers are of course considerably lower than those for YSZ (which is more than $100 /kg), which is one of the primary attractions for MSCs over their ASC counterparts.

As mentioned in the earlier sections, a porous substrate should be such that it has adequate porosity for permeation of gases it can provide the mechanical and structural support, and conduct electrons from electrodic reactions, while ensuring CTE match with the adjoining layers. Other key attributes include – resistance to oxidation, resistance to moist fuels, and of course, being inexpensive[6].

As indicated by Kesler et al.[30] porous metal structures can be used in various morphological forms, viz., foams, and meshes, or by laser drilling of holes in Ferritic steel blocks/ plates as done by Ceres Power, or by powder metallurgy processes (PM) which includes Pelletization, Spraying and Tape Casting. Kesler et al.[30] have also discussed methods to characterize porosity (Archimedes method, Hg-Porosimetry) and pore size distribution (Hg-Porosimetry), measuring the surface roughness (using surface Profilometry), and gas permeability (Gas Permeation rig with Mass Flow meter to measure flux across the substrate).[30] These are standard techniques used for characterization of porous structures and are universally applied – this review is focused on MSC technology, will not discuss some of these basic aspects. Instead, analysis of major developments reported further on, relating to the behaviour of metallic substrates under air and moist fuel conditions, their durability over time and ways and means of pre-treating them prior to the deposition of anode functional layers, and electrolytes.

The early work done by Ikerlan of Spain (Antepara et al.) (2005)[27], emphasized the importance of certain critical attributes necessary for porous supports, which can be quantified individually as part of component testing, and then integrated into the product. Component testing for metallic porous substrates, included - Mass Gain after air oxidation and Area Specific Resistance after air oxidation (4-point probe conductivity). This is beyond the other necessary attributes such as - Coefficient of Thermal Expansion (CTE), Creep and Mechanical strength, thermochemical stability in contact with ceramics (diffusion of elements between steels and ceramics) and the vaporisation of chromium in atmospheres in the presence of water vapour during the operating lifetime of MSCs.

Antepara et al.[27] (2005) compared Crofer 22® APU, AMETEK and also the Japanese ZMG 232, and their relative resistances to corrosion. In early data comparisons, Crofer 22® APU were more resistant to corrosion than the others. Plansee has discussed some of the properties of their ITM alloy (containing as much as 26% Cr, and a small amount of Yttrium Oxide) (2008)[25,] which was used extensively in work done by the German-Austrian consortium, reported earlier in the technology review section. The Area Specific Resistance (ASR)of ITM and Crofer 22® APU (Thyssen Krupp) as measured by a 4-point conductivity probe, is shown in Figure 25. The samples are subjected to oxidation in air, over time at different temperatures leading to Cr-oxide scale formation. The coating of ITM steel substrate with LSM deposited by PVD prevents loss of conductivity – the ASR is controlled to less than 2 mΩ.cm^2 although the oxidative pre-treatment of the ITM alloy between 200 and 500 hours causes very little increase in ASR. In comparison, Crofer® 22 APU, shows an increase of almost 20 mΩ.cm^2; ITM alloy is demonstrated to be much more stable (Figure 25) to oxidation

Figure 26 shows the rates of oxidation, as weight gain with time, for ICs of various thicknesses[25]. The samples had several preparation methods, with different surface finishes, viz., Ground, Rolled, ‘Vibratory Ground’. ITM alloys are claimed to have superior oxidation resistance. It is also important to limit ‘breakaway Oxidation’, i.e., which happens after the Chromium layer is depleted and the Fe is unprotected. ITM alloys show very limited ‘breakaway oxidation’ (Figure 26).

Meanwhile, Thyssen Krupp have discussed the newer alloy Crofer® 22H whose composition and properties are shown in comparison to Crofer® 22 APU (2010)[26] (Figure 27). The former has been designed for better creep strength, and suppression of oxidation. Thyssen Krupp’s data however show high ASRs for SS 446 alloy (24% Cr), compared to Crofer, at 800^{o}C. More detailed properties of Crofer® 22H, and a comparison with APU and other alloys, have been compiled by Sarasketa-Zabala et al.[28] (2012), shown in Tables 4 and 5.

While both the varieties are considered primarily for Interconnect applications, they can be used effectively for porous substrates as well. It is preferable to have ICs and porous substrates of the same material.

Prevention of Cr-poisoning, and resistance to air-oxidation are key targets for developing ICs, but more important to porous metallic substrates/ supports, is its stability under highly moist but reducing environments. Therefore, stability tests for Ferritic steels in H_2O/H_2 mixtures are essential for determining and improving durability of MSC cells and stacks. Further work by Ikerlan research teams (E. Sarasketa-Zabala et al.) (2012)[28] have therefore, specifically focused on the anode side – wherein the stability and reactivity of Crofer® 22APU was investigated under highly humidified hydrogen gas (50%) at the high temperature of 800 °C, which are extreme conditions for porous ferritic steels. Porous substrates with porosities in the range of 25 - 40%, showed stability towards moist Hydrogen for over 4500 hours. Much of the growth of scale appeared to occur in the first 100 hours – due to the formation of mixed Chromium oxide layers with some Fe and Mn, and resistance to ‘spalling’. Even after 500 hours, there was no further increase in the oxide scale growth and there was no decrease in porosity due to scale formation – the authors recommend over 30% porosity in the beginning, to prevent any diffusional limitations caused by the oxide layers forming on the walls of the pores, which will clog the porous pathways.

However, the quest for very inexpensive stainless steels that satisfy the basic requirement of CTEs and cost continues – SS430L continues to be very attractive in this regard. One example of the use of SS 430L substrates is by Xia et al.[29] (2012), who have co-fired yttria-stabilized zirconia electrolytes and 430L stainless steel substrates. Ni and doped ceria (SDC) were impregnated and calcined at lower temperatures, only in the end. Peak power density for cells made with 430L steel substrates, was as high as 246 mW cm^2 at 700^o C[29], and good tolerance to redox cycling was also demonstrated suggesting that this design is feasible for high performance metal-supported SOFCs. Ferritic steel substrates were prepared together with YSZ and with pore formers like graphite and PMMA and form the backbone of the anode. A 2nd electrolyte-only YSZ layer was spread/ distributed on top of the green bi-layer. Co-sintering was achieved partly in air till 600^o C to remove the fugitive pore formers, following by sintering in Hydrogen/Ar at 1400^o C. This is a little surprising given the fact that the melting range for ferritic steels are in the range of 1400-1500^{o}C. The authors claim to have a porous structure with a dense phase electrolyte on top of it without de-laminations or cracks (evidenced by OCVs of about 1.05 - 1.1 V) [29]. The cathodes were a mixture of LSM and YSB $(Y_{0.25}Bi_{0.75})_2O_3$, and applied to the electrolyte surfaces. Ni/SDC was infiltrated on the anode side - cells show redox tolerance losses of no more than 10% over 6 redox cycles – Infiltrated Ni appears to work, although higher redox tolerances are needed, and further testing of 430L is needed for proving its resistance to corrosion (moisture in fuel feed and to ambient air). There has not been much long term performance data yet on this cell, and that too in high moisture contents. However, this is an instance of a successful of a working cell on a ferritic steel substrate with the electrochemical layers deposited by conventional techniques.

Early studies (prior to 2010) by Molin et al.[31] show that porous SS 430L has reduced oxidation resistance both in air and in humidified hydrogen at 800^o C (Figures 28, 29). The high surface area of the porous substrates also enhances the oxidation, which follows the familiar parabolic character[6], with time. Under test conditions, Fe-oxide scale tends to form as well in air, whereas the extent of oxidation is lesser in humidified hydrogen, which shows only the protective layer of chromium oxide. During exposure to air, however, high weight gains are well correlated with reduction in electrical conductivity and with the observed formation of Iron Oxide (verified by XRD). For SS430 the modest Chromium content of 16-18 wt % does not provide enough Chromium oxide scale, particularly for a porous support, to prevent the formation of iron (iii) oxide. After about 75 hours of oxidation, the ASRs exceed values of 100 mΩ cm^2 which are entirely unacceptable, as per the authors.[31]

Ni-based Alloy substrates

Other materials for porous substrates, which include several Austenitic steels and other Ni-based alloys, have been studied extensively. The CTE mismatch between Ni and GDC or SDC or YSZ or ScSZ, can be detrimental to the durability of the cell. CTE of GDC is about 12.4×10^{-6} /K, compared to 16.5×10^{-6} /K for Ni. Upon alloying with Fe, the CTE can be brought down to about 13.7×10^{-6} /K when used at a mass ratio of 1:1. Tucker et al.[6] have commented upon the ease of usage of Ni and Ni-Fe – reflected by the large number publications using these materials as supports. However, the stability towards oxidation in air, and in fuel-moisture conditions is very poor for Ni and Ni-Fe[6]. Adding Fe to Ni can lower the cost, improve CTE, but will not make it resistant to oxidation. On the other hand, ferritic steels are low cost, have appropriate CTE match with the ceramic layers, and offer better oxidation protection than Ni-Fe and Ni systems. Ferritic steels can be coated appropriately to improve durability in fuel-steam environments. The only problem being the complexity in the overall cell manufacturing, which has been one of the principal areas of discussion for MSC technology.

Austenitic Stainless Steel Supports

Molin et al. in a series of articles[32-34] have investigated high Chromium, Ni-containing SS316 (16-18.5% Cr, 10-14% Ni) which also has Mo, Mn and Si. However, SS316 has a CTE of 16 ppm/K, which is totally mismatched with the 10-12 ppm/K values for ceramic layers.

SS316 has been clearly shown to form a mixture Fe, and Cr Oxides during air oxidation cycles at 800° C and Cr_2O_3 in humidified Hydrogen. Chromia scale formed in humidified fuel condition shows satisfactory electrical conductivity[32] although on the air side, advanced coatings are necessary not only for Cr loss but also for protection against oxidation.

Further work by Molin et al. (2010)[33] on comparison of three porous stainless steel substrates as possible candidates for the support of MS-SOFC - PI600, 317L and 430L; all three cases report about 16-18% Chromium, the Ni contents are very different – the CTEs (TECs) are closer to the ceramic layer for PI600 (Table 6)[39] whereas SS317L is much higher, as has been commented upon before. SS317L has no protection at all, despite having significant Chromium where as PI600 and 430L do show the presence of the Chromium Oxide scale. Based on the mass change and porosity change results, the 430L and PI600 stainless steels seem to be suitable for SOFC applications (the latter is a lot closer, for an Austenitic steel, to the ceramic layer, as shown in Table 6). However, both 430L and PI600 show high ASRs with respect to their oxide scale, and cannot be exposed to air under operating conditions at 800^o C.

Molin et al.[34] have recently (2015) studied IN625 Austenitic steel alloy as well, which has 20-23% wt Cr, >58 wt% Ni, < 5 wt% Fe, and a variety of micro-alloy components (Table 7)[42]. IN625 (Inconel 625) porous substrates (20-23% Cr, over 50% Ni) (Table 7[34]) were tested for high temperature corrosion, in both air and in humidified Hydrogen, at temperatures from 700 to 800^o C. As expected, the rate of corrosion in air is higher than in humidified Hydrogen. Corrosion rates can be reduced by infiltrating rate earth elements such as Ce, Gd, La and Y. Molin et al.[34] have elicited a very simple impregnation (infiltration) technique for the rare-earth elements, using nitrates of Cerium, Gadolinium, Yttrium and Lanthanum, which were dissolved in ethanol, prior to infiltration. The weight change after calcination was no more than 1% of the infiltrated Rare Earth Oxide. The SEM data shown below in Figure 30 illustrates the corrosion resistance brought about by the infiltration process.

A comparison of the thickness of the oxide scale formed after 1000 hours at 700^o C reveals a huge reduction in corrosion rates, particularly when Y is used (where there is a reduction by a factor of 50). While there is no conductivity measurement data or cell testing data, yet, this type of approach wherein one does not have to look for a very expensive ‘magic alloy’, and can merely modify the surface with strategic coatings, is very promising.

Kesler et. al.[47] have used sol gel techniques to also generate protective coatings for Ferritic steel and make them oxidation resistant. La, Y and Ce Oxides (Rare Earth, RE) were infiltrated into the porous ferritic steel matrix, by first forming a precursor solution with ethylene glycol, and nitric acid, and then by deposition/ infiltration into the porous metallic matrix by a repeated process of dip coating and drying/calcination (400^{o}C). After a final calcination step at about 650^{o}C, the rare-earth oxides form on the surface of the metallic substrate. The dynamics are explained in detail in this reference. The RE oxides are considered Reactive Elements[47] which undergo reaction with the Chromium, thus forming a conductive coating. The aim of this approach is to preserve the stability of the porous substrate while ensuring adequate conductivity of the backbone structure. La_2O_3 and Y_2O_3 coatings showed better performance than CeO_2 coatings in protecting alloys from oxidation, from detailed Oxidation/ weight gain experiments. However, this strategy may be very effective in protecting ferritic steels like SS430L (used in this reference[47]) under high moisture conditions in the anode.

In what appears to be a manufacturing-friendly and recent effort (2015) to form a metal supported cell, a Ni-Mo porous alloy[35] is chosen as the support, with an anode which is composed of LSCM and LDC-NiO anode, LSGM electrolyte, SDC barrier layer and SSC cathode, all deposited by sequential Atmospheric Plasma Spray techniques (Yang and co-workers[35]). The method for substrate formation has described very precisely by Yang et al.[35] which includes – spray drying of Ni and Mo particles to ensure a consistent particle size distribution. The powders are filled into a steel mold of appropriate size and compressed at about 35 tons of load. Sintering of the powders in hydrogen at 1200^{o} C with a pyrolyzable filler (pore former) completes the cycle for the porous substrate formation. Cell performances in Hydrogen atmosphere are impressive – about 1 W/cm^2 at 0.6 V at 700^{o} C.

Ni-Al porous substrates were tried out recently by Solovyev et al.[36], (2015) as a variation to some of the NiCrAlY systems reported by Tucker[6]; Ni-Al powders were prepared in-house by a combination of a sintering step similar to ‘pack-cementation’ and combustion synthesis process and annealing at 1300^{o}C in Ar. Ni_3Al and NiAl phases were the dominant compositions, and the final porous structure had 27% porosity with an average pores size of 5 microns. The formation of the alloy containing about 20% aluminum is more stable to shrinkage at 1200-1300° C, can be sintered to as high as 1300°C in Ar atmosphere, which allows for the sintering of the electrolyte phase at a higher temperature. NiO-YSZ anodes were coated by screen printing effectively, although during sintering of the half cell in Argon, partial reduction of NiO occurs, and Ni particles tend to agglomerate. The CTE of Ni-Al substrates (15 ppm/K) is mismatched with the ceramic layer, but the degradation of the interfacial layers has not been observed, over a 100-hour operating period, which could be due to the porosity of the metallic support.

On to this porous substrate layers were deposited, the NiO-YSZ anode layer by screen printing initially, followed by YSZ electrolyte by RF Magnetron Sputtering, interrupted every 20 minutes by electron beam 'treatment'. The electrolyte thickness was reported to be about 10 microns. The cathode deposition was done simply by a process of screen printing, and in-situ sintering at about 850° C. Figure 31 demonstrate the cell performances of cells with Ni-Al support[36]; at 0.7 Volts, a maximum power density of about 350 mW/cm^2 can be reached, at cell operating conditions of 800°C, 150 ml/min of Hydrogen flow and 450 ml/min of air flow. Further optimization on microstructure is to be done, as the authors indicate, but the Ni-Al support is another alloy scaffolding that has been shown to be effective (microstructure shown in Figure 32). The only issue that has not been commented upon in this article is the stability of the Al containing substrate, towards oxidation, under high moisture levels. Performance data reported in this publication is with dry Hydrogen. Al tends to form a protective Al_2O_3 layer in the presence of moisture or air or both, which is non-conductive and this could lead to more Ohmic resistances in moist feeds[6].

Alloys for Interconnects (ICs)

The differences in the attributes for ICs vis-à-vis porous substrates are quite simply that ICs are dense, and tend to generate Cr-oxy-Hydroxide vapor in air, thereby poisoning the adjoining cathode – whereas the anodic porous substrate is not exposed to air, but only to moist fuel. The latter case will deplete the Chromium over time, as a protective Cr-film that grows in thickness, as discussed extensively in the previous section – it is therefore a matter of which degradation mechanism plays the dominant role. The issue of CTE match with the ceramic layers is not the most crucial, since sealing schemes, and stack design can ensure that the ICs are not contacting the ceramic layer, intimately. Usually ICs are separated from each other by sealing (conventional cells, ESCs or ASCs) or are welded/ brazed to the substrate (MSCs) which is usually of the same metal. Many dense metal candidates are available for IC applications – Crofer® 22 APU, Crofer® H, ITM, ZMG 232 and SS 430 L, among Ferritic steels. Crofer® 22 APU is widely used in conventional SOFCs as the IC with cathodic coatings to prevent Cr poisoning. If coatings are to be used on the cathode, it is tempting to use cheaper IC materials as well such as SS430L. On the anode side, SS430L ICs will also be exposed to spent fuel with high moisture levels – this is a similar situation to that encountered by porous steel substrates, and solutions such as protective coatings can be implemented in the same way for ICs too.

During evaluation of the IC, similar testing methods (described earlier) are used to check for corrosion stability, i.e., weight gain tests using cyclic oxidation protocols at about 800^o C, and 4 point conductivity testing to examine conductivity of the oxide films that tend to form on the surface in air, and in steam/H_2.

Most developers continue to use Ferritic steels for IC applications[7-20]. Since the IC development is 'across the board' extending to all kinds of cells, developments in ICs and coatings, have not been discussed very much in this review. Only coatings on porous metallic substrates are discussed further, as part of manufacturing operations.

REVIEW OF ADVANCED MANUFACTURING AND CELL-STACK INTEGRATION

Manufacturing techniques hold the key to significant cost reduction for MSCs – having significantly low materials cost will not amount to much if it is not backed up by similar cost-effective manufacturing techniques. The latter must evolve to highly automated and precise set of operations capable of generating high throughputs. Typical techniques that can be scaled up are – tape casting (TC), screen printing (SP), Thermal Spray, and colloidal deposition, viz., Inkjet Printing, electroplating/ electroless plating, for deposition on surfaces; which is followed by high temperature sintering in furnaces, although thermal spray, e.g., Atmospheric Plasma Spray and its variations in terms of vacuum and low pressure, Spray Pyrolysis offer major possibilities in a combined deposition and sintering mode, due to the short time scales involved to complete the sintering / co-sintering [37-46, 55-56, 74-76].

Hui et al.[37] in a comprehensive review, have discussed the technology of Thermal Sprays in general, including the widely used Atmospheric Plasma Spray. Plasma Spray (PS) technology has been used extensively for coatings for turbine blades, components of diesel engines, for example, where protection of crucial metallic parts with ceramic layers, are necessary, to protect them from wear and tear, and corrosion. The extension of PS (or Thermal Spray) to SOFC coatings is an example of cross-fertilization across applications, and can give a near dense and integral electrolyte layer with ceramics like doped ceria[36]. Hui et al.[37] have described the methods for plasma spray, along with the principles of operation, i.e. generating the extremely high temperature plasma 'plume' using high voltage, and using inert gases with Hydrogen in variable proportions to control the temperature of the plume. There is a delivery system of particles into the Plasma Zone, whereby particles undergo melting, and travel via the plasma jet onto a target, where they cool and solidify, as they hit the target (the target can also be cooled to adjust the surface temperature). A similar delivery system can be designed for or suspension or solution plasma spray. Plasma zone temperatures are easily over 6000 K, although the temperature of the target can be usually in the range of 1000-1500° C. A significant advantage is the short 'processing' time for a deposition on the sample, in the plasma region, which enables high throughputs – of nano powders and coatings. YSZ and LSM powders of particle sizes < 100 nm have been marketed for niche applications.

In comparison with the traditional ceramic processing methods in SOFCs which include – tape casting, screen printing, spin coating, furnace sintering[47], PS has the potential to minimize processing costs, due to usage of lesser equipment, high volume of production, easy scale up, although the lack of precise control in the ceramic microstructures is under development. In SOFCs, while plasma spray can be used for deposition of cathodes, anodes, barrier layers, IC coatings and electrolytes, it is the last one that can make a big impact in case of MSCs. Electrolyte layers can be deposited either via PS or via screen printing on pre-sintered porous metallic substrates in several cases (or even without the anode functional layer pre-deposited and sintered) [6], but 100% densification of the electrolyte layer is not easy to accomplish, as green density obtained by wet colloidal deposition is not sufficient for the half-cell layer to be sintered at 1200° C or less, at which the porous substrate was sintered – the only exception being Ceres Power's 1000° C air-sintering technology. Even in situations where researchers have used Spray Pyrolysis, where annealing is required for densification, 1200°C is shown to be necessary for total elimination of porosity[38], at least in the case of YSZ and GDC. One of the problems as highlighted by Scherrer et al.[38], from ETH Zurich, is that porosity tends to form, as and when salt precursor and additives decompose during the deposition and subsequent annealing.

However, the technology associated with the deposition of 'molten' electrolyte powders from the plasma zone, hitting the target substrate along with the plasma plume, can be far more effective than the conventional 'ground up' aqueous/ organic deposition of powders on substrates, followed by a slow high temperature cycle in a furnace. The authors of this review[37] have emphasized that APS (Atmospheric Plasma Spray) can work effectively to deposit electrolyte powders on metallic substrates. Moreover, there are variations in plasma spray as well – the traditional Powder plasma spray (PPS, specifically; in most cases APS automatically refers to PPS) where flowability of the powders is important – achievable by partial sintering of as-received electrolyte powders, followed by pulverization/ crushing, thereby generating flowable powders (typically around 100 microns for GDC[58]. Suspension Plasma Spray (SPS) wherein powders are dispersed finely in a liquid and injected into the plasma zone, Small Particle Plasma Spray (SPPS), which involves spraying of nanoparticle powders, and spraying molten particles under reduced pressures (Vacuum Plasma Spray, VPS).[37] Further along, in the article, more examples are provided showing the efficacy of Plasma Spray coatings for electrolytes, cathodes and anodes on porous or anode-coated porous metallic substrates.

APS also offers tremendous scope for an ‘assembly line’ type production – further emphasized by Kesler et al.[42-47] as it can be implemented either using powder or by slurry or by precursor solution. Developments in Atmospheric Plasma Spray (APS) towards achieving better plasma plume (flame) control are in progress, in a bid to lower the operating and CAPEX costs associated with Vacuum Plasma Spray (VPS) techniques. Table 8 catalogues a comparison of processing techniques like PLD when integrated with Plasma Spray – for cases where the electrolytes are bi-layered[46]. The latter has been used extensively by DLR in its SOFC multi-layer deposition processes, but they too integrate plasma spray with PVD and Magnetron techniques as they go to less than 2-3 micron thicknesses. Typical Plasma Spray Parameters used by Kesler and co-workers (2009)[55] using Suspension Spray (SPS) for electrolyte deposition and regular powder spray deposition for the anode and cathode are shown in Table 9.

Further variations[43] in operating conditions are reported below, by Kesler et al. (2011), in Table 10. Early work[42-44] indicated high surface roughness, and cracks in the surface, leading to poor cell performances in the 650-750^{o}C (OCVs from 0.9 to 1 V), on YSZ electrolyte cells with SS430L Ferritic steel porous supports (2009-2011). There has been tremendous evolution in optimization of Plasma Spray techniques, reported by the same author [23, 24, 47, 74-76], culminating in some very high performances mentioned earlier in the technology development section, and in Table 11.

The usage of plasma as merely a heat source, i.e., ‘Plasma Glaze’, like a Rapid Thermal Processing which was experimented at NFTDC, Hyderabad in collaboration with University of Cambridge, UK [56] offers a very quick turnaround time – in fact the maximum time spent by a sample undergoing treatment under plasma could be no more than 5 minutes. The operations for deposition of electrolyte and anode on porous SS430L, and for the cathode are entirely carried out in air. The only step taking place in reducing atmosphere is the preparation of a porous SS430L substrate.

The combination of APS with High Heat Flux technique (‘Plasma Glazing’), in conjunction with colloidal deposition of anode functional layer and cathodic layer, [56-58] can have a huge impact in achieving high throughputs, and in lowering manufacturing costs. For example, a simple cell-sintering protocol comprising – substrate preparation, APS deposition of an anode functional layer, APS deposition of the electrolyte layer, followed by the cathodic layer, can be accomplished. There are two complexities that do emerge that need to be resolved prior to generating a commercial process for MSC production – one being, the need for barrier layers. It has been shown earlier [12-15] that barrier layers which are typically about 1 micron are used to enhance durability and minimize degradation. Layers with such low thicknesses, are difficult to achieve by APS, and in the examples shown earlier, techniques such as PVD and/or Magnetron sputtering are being used. The latter techniques rely on vacuum, and are expensive in comparison to atmospheric operations. Barrier layers of higher thicknesses which are typically achievable by plasma techniques invariably add to the resistance of the cell. To avoid depositing Barrier layers, we may need to perhaps re-visit our understanding of the interfacial changes both at the support-anode interface and at the electrolyte-cathode interface, and find ways to minimize degradation.

The other issue that needs resolving is that APS and its variants, have at best, generated about 1.10 V OCV reported[23], which is a clear indication that competency in manufacturing has not yet been achieved to a near-100% level, i.e., manufacturing a 100% dense ceramic electrolyte layers.

This area offers immense scope for advanced research – whereby the microstructure of a splat geometry, can be modified by adjusting process parameters and operating conditions, and possible re-engineering of the deposited ceramic.

Other strategies for deposition of electrolytes, protective coatings, barrier layers and electrodes include – Sol gel coatings[47, 60], PVD, RF Magnetron, Gas Flow Sputtering[12-15,60] traditional co-tape casting, and co-firing[49,50, 53, 61], Phase Inversion preparation process[51], and some innovations such as Powder extrusion Molding, as well[48].

Barrier Layers

Barrier layers must have sufficient electronic conductivity, porosity and CTE compatibility with contiguous layers, and be very thin, typically 1-2 microns, to minimize all non-electrolytic Ohmic resistances. Much of the work has focused on – La-Chromates[36], GDC[36, 62, 76], SDC[76]. These materials have been used both in the anode as well as in the cathode, where there is the possibility of interaction of species such as LSCF with YSZ at the fabrication temperatures of about 1000°C or so[63], which are typically used.

Techniques such as electron beam evaporation (EB-PVD) yielding about 0.5-1-micron layer of GDC, and reactive spray deposition (RSDT, in air, < 2 micron) of GDC for comparison, highlighted in the work by Julich-NRC-UCONN (2011)[62] are being used to obtain the barrier layer that satisfies the stringent requirements. Over a 5-hour test at 900°C the authors[62] demonstrate that inter-diffusion of Ni against Fe and Cr, are prevented in this time, although the performance of a full cell has not been discussed in this work.

The early work on diffusion barrier layers (DBL) such as Cr_2O_3/ Cr_2MnO_4, GDC and Ceria[65], deposited by vacuum Plasma Spray methods on the anode side, on a MSC comprising – FeCr substrate, Ni-YSZ anode, YSZ electrolyte and LSCF cathode, gave about 430 mW/cm^2 at 0.7 V, at 800°C, in the case for ceria as DBL. A 165-hour test carried out at constant current of 0.3 A/cm^2 showed stable operations and no degradation. However, after further operations, 'break-away' oxidation of the Fe-Cr substrate resulted in degradation and huge diffusional resistances – although the causes for it are specific to the experiment and not generic for the substrate.

Other instances of barrier layers on the cathode side of the MSC are reported by Bae et al. (2010)[64] and Kesler et al.[76] where variations are made in the deposition of either GDC or SDC, respectively. Bae et al.[64] clearly report the loss of performance of YSZ cells without use of cathodic barrier layers (from 0.81 W/cm2 maximum power density to 0.63 W/cm2, over a 50-hour period, at 800°C), even upon exposure of the YSZ to the unsintered BSCF cathode, at temperatures as low as 800°C. This is attributed to the formation Sr and Ba Zirconates, which were discussed earlier. The authors use BSCF cathodes as well, and have experimented with unsintered cathodes, and sintered cathodes with unsintered GDC barrier layers. Maximum power densities of about 0.78 W/cm^2 were achieved at 850°C for 'un-sintered' BSCF cathodes, when used with an un-sintered GDC barrier layer – it is claimed that the use of the GDC barrier also enhanced the adhesion of the cathode to the electrolyte and boost performance, and lowers degradation, as observed from a 1000-hour run. The GDC barrier thickness is maintained to < 1 micron, for optimal performance. Further extension of this work towards optimizing cathode performance is discussed in the next section.

Kesler et al. (2016)[76] have prepared barrier layers (SDC) by Suspension Plasma Spray deposition, with thickness of about 2 microns, on the cathode side. From EIS data on symmetric cells, in some cases, over time, they have demonstrated the stability induced by the deposition of the barrier layer, at 750°C for YSZ cells. Much of this work is towards characterization of symmetric cells, and the resolution of their EIS spectra – any form of plasma spray deposition of ultra-thin barrier layers, if successful, may provide to be a boost toward facile cell manufacturing.

Strategies for deposition and stabilization of cathodes

The complexity in terms of manufacturing as already been discussed. On one hand the substrate, anode, electrolyte is usually sintered together – under reducing conditions, whereas the cathode layer has to be then deposited in the end, and sintered in air, keeping the rest of the cell (particularly the metallic support) under reducing conditions. One can, as demonstrated in several papers referenced here, sinter the cathodes in-situ, i.e. prior to cell operations at the temperatures of interest, the cells can be kept at a higher temperature (900 to 1000°C) for a typical short time, allowing the cathode to sinter and bond with the electrolyte – during this operation, however the anode side would be under reducing or inert conditions which prevents porous metallic substrate from oxidation. It is also very likely that during this period, considerable coarsening/ agglomeration of Ni may occur, since NiO → Ni transition has already taken place during the sintering of the half cell in reducing atmosphere.

Plasma Spray of cathodic powders[76], or providing Plasma Heat[58] alone after colloidal deposition, are viable methods for cathode deposition, once the half-cell has been fabricated. By using Plasma Spray (suspension) one can also deposit the cathodes (LSCF) with carbon pore former (Kesler et al.[76]), and introduce barrier layers (SDC) between the cathode and the electrolyte as well, in a bid to lower the

ASR of the cathode, and to prevent chemical interaction between the electrolyte and the cathode. Very low ASRs of about 0.062 Ω.cm^2 were reported, at operating temperatures of about 744°C as well[76].

Kesler et al. have used 'axial injection' plasma spray[74] and 'Solution Precursor' Plasma Spray[75] variations of Plasma Spray methods to deposit Ni-YSZ anodes with controllable pore sizes/porosity using carbon black pore formers as well. The cell fabricated entirely by axial injection plasma spray has shown to give 1.13 W/cm^2 maximum power density at 850° C. Solution Precursor Plasma Spray deposition of Ni-YSZ anodes, are shown to generate about 0.52 W/cm^2 at 750° C in humidified Hydrogen.

To ensure stability against reduction, and with a view to generate higher cathodic activity for intermediate temperature applications, newer materials have been investigated recently. Vibhu et al.[67] (2015) have continued their characterization and stability studies on Nickelates which are known to be stable under reducing conditions. $La_2NiO_{4+\delta}$ (LNO) are stable under reducing conditions, and $Pr_2NiO_{4+\delta}$ (PNO), offer high electrochemical activity. Mixing the two materials as $La_{2-x}Pr_xNiO_{4+\delta}$, mixed nickelates were synthesized (LPNO), and studied as possible oxygen electrodes for solid oxide fuel cells (SOFCs). Electrochemical characterization of half-cells[67] confirmed the following –

i. The ratio of La/Pr, as determined by x, strongly determines electrochemical performance, e.g. La rich phases ($x<0.5$) may provide higher stability while $0.5<x<1$ generates better performance (lower ASR).
ii. All the lanthanum–praseodymium nickelates are over-stoichiometric in oxygen in the whole temperature range (up to 1000°C, from TGA data) in air and in Argon.
iii. Other properties such as - electrical conductivity, CTE's, oxygen diffusion and surface exchange coefficients appear to be adequate for the application of LPNO for MS-SOFCs.

In this work however, cell performances have not been carried out yet, and this may be another significant step towards achieving higher performances in the 600° C temperature ranges for MSCs.

Other methods to solve the requirement of cathode sintering are quite simply – using 'un-sintered' cathodes[64, 66] and subjecting them to process/ operating conditions. BSCF ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$) is known to sinter at lower temperatures. To improve adhesion to the electrolyte and to improve performance durability with time, Bae et al. (2010)[64] added a buffer layer between the 'unsintered' cathode and the electrolyte, of varying thicknesses – from 1 micron to 6 microns. Like the cathode, the buffer layer can either be sintered, or un-sintered. The authors report increased polarization (from EIS experiments) as buffer layer is increased in thickness, and slightly better cell performance (0.76 W/cm^2 for un-sintered buffer layer to 0.82 W/cm^2 for sintered buffer layer); however, sintering of BSCF improves performance to 1.23 W/cm^2 at 800^{o}C, as shown in Figure 33, with microstructures shown in Figure 34.

Bae et al.[66] (2011) have compared BSCF performance with 'unsintered' LSCF ($La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$) and LSM ($La_{0.8}Sr_{0.2}MnO_{3-\delta}$), without using any buffer layer, and claim acceptable performances. BSCF and LSCF coated cells show similar performances whereas un-sintered LSM exhibits very poor performance, revealing poor sinterability under operating conditions (800^{o}C). Metal supported BSCF-Cells (STS430 plates with flow channels) show a power density of about 0.74 W/cm^2 under the same operating conditions and shown in Figure 33.

Infiltration of cathodes and anodes into porous scaffolds/substrates which were done and reviewed by Tucker et al.[6], continue to be pursued by many research groups. Zhan et al. (2014)[69] have fabricated cells with a porous SS430L support, coated with dense YSZ electrolyte (about 20 microns thick) and followed by porous YSZ as a cathode scaffold. They have used $SrFe_{0.75}Mo_{0.25}O_{3-\delta}$ (SFMO) as both anode and cathode catalyst, both of which are relative new materials, having never been used in commercial SOFC applications. SFMO is infiltrated both in the cathode and anode side, after the triple layer mentioned above has been fired in a reducing atmosphere. These cells show maximum power densities of 0.74 W/cm^2 at 800^o C in moist hydrogen and 0.4 W/cm2 at 700^{o}C. Along similar lines a Redox-stable $La_{0.6}Sr_{0.4}Fe_{0.9}Sc_{0.1}O_{3-\delta}$ (LSFSc) oxides are introduced as symmetric electrode catalysts by Zhan et al.[70], reporting about 0.65 W/cm^2 maximum power density (voltages.). EIS data

Impedance analyses (EIS) on symmetrical cathodes and anodes show that the anode polarizations represent the largest losses while the cathode polarizations make negligible contribution to the overall polarization. The authors proceed along the next logical step, i.e., replace the LSFSc by Ni in the anode side [Ni $(NO_3)_2$ solutions impregnated into the porous SS 430L substrate, and calcined at 600°C for 1 h in 5% H_2-95% N_2][71]. Maximum power densities of 907 mW/cm² at 800°C were observed although, continuous degradation in performance is observed, even at 650°C and 0.7 V during a 200-h durability measurement. This is predictable since infiltrated Ni is known to coarsen easily and counter-diffuse with the ferritic steel substrate. In the next step (2014)[72] the authors now use Ni-YSZ as the anode and generate about 438 mW/cm² at 800° C, which is considerably lower than before (due to higher anodic polarizations measured by EIS). Infiltration of Ni-cermets require further stabilization as was discussed by Tucker[6], to maximize the performance. It is also imperative that the counter diffusion between Ni and Fe/Cr be minimal, since it is not very easy to introduce a barrier layer in an infiltrated cell morphology

New cathode compositions such as $(Bi_2O_3)_{0.7}(Er_2O_3)_{0.3}$-Ag composite (2013)[77], $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta}$ (2016) [78] and a new aerosol deposition technique for LSM-YSZ cathodes (2016)[79] are among the more recent developments in the choice of materials and fabrication techniques for MSCs (Refer to Table 11 for the summary of data).

Sidebar title

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Conclusion

Over the past 6 years, considerable R&D work continues to be done in the areas of Metal supported SOFCs. A very thorough examination of literature during this time reveals that efforts have been made at several levels – basic R & D, manufacturing and stack build. The reviewer, in this article is primarily interested in the more viable paths towards commercialization, and has thus put premium on manufacturing techniques. Therefore consideration of approaches towards manufacturing, undertaken by academic research groups vis-a-vis technology organizations/ companies have taken precedence in this review. The inherently simple tape casting, screen printing and co-firing methods to make the Substrate-Anode-Electrolyte 'half-cell' are still being used widely – and the researchers have tailored other operations around them, e.g., Ceres and Topsoe.

In terms of commercialization, only Ceres Power has reached a state of cell/stack and system marketability (TRL levels of 8 and above). The work done by major consortia – DLR/ Plansee/ Julich/ KIT (Germany-Austria), Topsoe/ Riso/ DTU, U. Toronto, Ramses EU partners (CEA-LITEN, CNRS, Sintef, Ikerlan, SOFCPOWER, Hoganas, and Baikowski) at stack and advanced cell levels, (reviewed in this article) has shown several manufacturing pathways and combinations of one or more of the following methods – Thermal and Plasma Spray and its variations, Tape casting, Screen Printing and co-sintering, Sol-gel and Dip coating, Magnetron Sputtering, PVD, Infiltration, Ink-jet printing, and Plasma Heating.

While Tape casting and Screen Printing are always applicable in one form or the other and may form the part of the manufacturing cycle, a few problems are not easily solved – electrolyte deposition and densification, and deposition of ultra-thin barrier layers of sub-micron thicknesses in a cost effective manner. One must deal with the requirements of – low temperature electrolyte sintering, improved durability of the cell by using barrier layers, and of course sealing and ICs (which are issues facing the SOFC community in general and not unique to MSCs). To lower production costs, mass manufacturability is most sought after and can be achieved by either by tape casting, screen printing, and other forms of colloidal deposition, OR by entirely moving towards thermal spray methods (Plasma Spray and its derivatives, Spray Pyrolysis). Many groups also focus strongly on infiltrating a porous matrix with active anode and/or cathode electrocatalysts (as the case may be) as a final stage. This is still a good option for laboratory work, although there are alternative deposition methods and it is not clear if wet methods and infiltration are the best, in terms of high throughput requirements.

One significant feature that is usually part of the MSC architecture, and generally not essential for the all ceramic cell, is the Diffusion Barrier Layers - these are essential in MSCs, and have been achieved by some of the research groups mentioned above, effectively, by very sophisticated vacuum techniques (PVD, Magnetron techniques, which may not be easily scalable and will add considerably complexity to the manufacturing cycle). Usage of 2 such barrier layers – one being a ‘diffusion’ barrier in the anode preventing Fe, Cr and Ni counter diffusion and the other being a barrier layer preventing interfacial reactions between YSZ and LSCF is essential for durability, although it is conceivable to explore 600^{o}C operations with GDC electrolyte and without the complexity of the barrier layer. Ultra-thin barrier layers have been deposited by advanced vacuum techniques (discussed earlier) - atmospheric operations are very facile and inexpensive, but they need rigorous optimization and control to achieve the desired texture and properties.

Plasma Spray (Atmospheric Plasma Spray) deposition which is primarily an atmospheric technique has shown considerable progress in densification of electrolytes, e.g., OCVs of about 1.1 V, which in the reviewer’s opinion remains the key rate determining step in marrying the twin objectives of cost effective manufacturability and high quality electrolytes within the cell. However, Plasma Spray may not be able to provide ultra-thin sub-micron barrier layers which are necessary at the anode and sometimes in the cathode side. Hence this could be a major area for continued research with a direct focus on a workable and durable product.

Novel options such as Inkjet Printing can be tried for depositing barrier layers[56-58], since they can be made at the 1-2 micron levels, but this is clearly work in progress. The need to develop an ensuing sintering step is still to be worked out but novel concepts such as Plasma Heating of surfaces (equivalent to a Rapid Thermal Processing), hold promise.

Academic groups continue to work on alternative metallic substrates (not Ferritic steels), e.g., Ni-Fe oxide systems, which can simply be manufactured like a ceramic cell, i.e., multiple air-sintering operations, with a final in-situ anodic reduction. There are a lot of data available here with Ni-Fe and Ni substrates, showing excellent power densities for button cells. However industrial groups have not focused much on Ni-Fe porous substrates, since they have poor redox characteristics. Even new developments like Ni-Mo and Ni-Al have not really been examined for their redox ability, and thus, long term durability.

Instead, ferritic steels (SS430L, Crofer, and ITM) continue to be the dominant substrates for cells, and as part of major stack building efforts. Within the family of Ferritic steels, SS430L is being explored as a viable candidate for porous substrates, notwithstanding its lower Chromium levels in comparison with Crofer and ITM. There is strong urge to develop 'Reactive Element' coatings, wherein the porous substrate is protected against Cr-loss in the form of thin protective conductive coatings. Given the fact that SS430L (or any SS400-ferritic steel) is perhaps one of the most inexpensive materials that satisfies the CTE match with the ceramic, it emerges as a particularly strong candidate for MSC technology.

The MSC community should therefore be very focused towards advancing manufacturability and to generate a wholesome manufacturing cycle, that is cost effective. We have reached a stage, wherein most of the materials are well known, and barring some innovations towards cathodic materials, much of the innovations are in engineering with the possibility of high impact. MSCs have immense potential in vehicle APUs – trucks, aircraft, long haul trains, and preferably in the 600-650^{o} C range, although from a cost perspective, they can make a significant impact toward the next generation of stationary decentralized power.

A review of the technologies (except for Topsoe/Riso/DTU and PSP/LBNL), reveals a much stronger shift towards thermal spray techniques, as evidenced by the German Consortium, U. Toronto/ NRC. Ceres Power uses screen printing even for the electrolyte. One major challenge is to deposit very thin barrier layers in the cathode and the anode, e.g. between the metallic porous substrate and the anode, and between the electrolyte and the cathode – in many applications, these may be necessary to prevent counter diffusion and formation of non-conductive interfaces on the cathode side, and loss of active

Ni from the anode, and contamination by Fe/Cr; these contributed to degradation and must be tackled for long term stable operation. Barrier layers are of the order of 1-2 microns, for which PLD and PVD type of very precise techniques are necessary – as of now, these may add considerably to the challenges of cost effective manufacturing. Effective long term performances that achieve the stringent targets proposed by the DOE (<0.2% degradation in 1000 hours), have not been shown so far, in the literature available in public domain – the best available data being 0.3 - 0.45 %/ khr for up to 6400 hours by Ceres Power.

In summary, MSCs are better suited for 600° C operations, primarily, because the redundancy that needs to be built in (barrier layers, higher levels of Cr in steel, porous substrate coatings) for higher temperature operations, will likely increase the cost of production. On the other hand, an operating the stack at about 600° C may not be conducive for total or even partial internal reforming on the anode side, which will impact electrical efficiencies. Cathode activation at such low temperatures is a problem as well, and these constraints should be addressed further till an optimum 'sweet spot' is established that reaps the benefits of lower Capital Costs and lesser degradation, and 'manages' the lower efficiencies that go along with it.

Notes

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Basic Introduction

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Figure captions

Figure 1: Schematic of cell architecture, LBNL work

Figure 2: PSP's VOTO product

Figure 3: Early cell performance data for Hydrogen, for Ceres Power (~ 2004)

Figure 4: Architecture of the cell with IC and porous metallic substrate[12]

Figure 5: Cassette with the cell enclosed and sealed within[12]

Figure 6: Cell Stack Assembly Fabrication (Plansee Consortium); Reproduced with permission

Figure 7: I-V data of 10-cell stacks (DLR-Plansee-ElringKlinger combine); average power densities of 306 mW/cm^2 (Vaccuum Plasma Spray, VPS) and 222 mW/cm^2 (Low Pressure Plasma Spray, LPPS)

Figure 8: Microstructure of Next Gen MSCs[13]

Figure 9: I-V data for Next Gen MSCs (H_2/Ar)[13]

Figure 10: Observe the slightly lower OCVs for MSC cells in a stack comprising of both ASCs and MSCs[13]

Figure 11. Different cell configurations of a sintered MSC concept, Gen A: original sinter concept, Gen B: novel thin-film concept with improved electrolyte and anode structure [Ref: Ni → Nickel; 8-YSZ → 8 mol% Y_2O_3-ZrO_2; CGO (GDC) → $Ce_{1-x}Gd_xO_{2-\delta}$; LSCF → $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$; DBL → diffusion barrier layer; ITM → P/M FeCr-based alloy (ITM-alloy from Plansee)]

Figure 12: Manufacturing cycle developed by the Plansee Consortium[14]

Figure 13: Microstructure of Gen B Cell, in the region around the electrolyte – showing thin dense phase

Figure 14: Testing MSC standard Cells[15] with diesel reformate gas using anode recycle configuration

Figure 15: Performances of advanced metal supported cells[15] – non- graphitic cells with LSCF and advanced anode structure show the highest performances; Reproduced with permission …

Figure 16: Half cell (without cathode and barrier layer) cross section (BSE image) – shows the infiltrated electrocatalysts nano-particles, with a higher concentration of nano particles closer to the support-electrolyte interface; Electrolyte thickness is about 12-13 micron.

Figure 17: I-V curves for anode electrocatalysts (Ni-CGO); fuel used is 96% Hydrogen with 4% moisture, and air on the cathode side; T = 650^{o} C[18].

Figure 18: I-V characteristics at 700^{o} C (average voltage/cell vs current density; total power from stack vs current density)

Figure 19: Average voltage per cell in an MSC stack; sample period of 150 h at 700 °C and 230 mA /cm^2

Figure 20: Half Cell architecture developed in the METSAPP program[20A, 20B]

Figure 21: Tubular metal supported cell data, I-V curves (Ramses Project)

Figure 22[23]: SEM micrographs for Ni-YSZ/YSZ/LSCF-SDC cells, where anode, electrolyte and cathodes were deposited by Atmospheric Plasma Spray technique

Figure 23: Left: Evolution of OCV over time, using refinements in APS; Right – Recent Cell performance (2013) of cells fabricated by APS (OCV = 1.09 V, at 750° C)

Figure 24: I-V curves showing the effect of types of Plasma deposition of anodes on performance

Figure 25: ASR tests on Crofer and ITM alloys[27]

Figure 26: ITM vs Crofer ICs: 'Breakaway'Oxidation[27]

Figure 27: ASR for key alloys as a function of air oxidation[28]

Figure 28: Mass gain in humidified H_2, with time (function of pre-sintering temperature)

Figure 29: Electrical conductivity for SS430L, after oxidation over several hours

Figure 30: SEM of cut cross section, A – no rare-earth infiltration; B – Y infiltrated; C – Gd infiltrated samples (1000 hours, and 700° C) [42]

Figure 31: Performance curves of button cells made from Ni-Al support in Hydrogen[36]

Figure 32: Microstructure showing functional and support layers for Ni-Al supported SOFC[36]

Figure 33: Performance of Un-sintered and sintered Cathode (BSCF) with Un-sintered and sintered Barrier layer (GDC)[64]

Figure 34: Microstructures of Un-sintered cathodes with Buffer layer[64]

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