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**Trends in the Processing & Manufacture of Solid Oxide Fuel Cells**

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Abstract

Electrochemical devices based on solid state ceramic materials such as solid oxide fuel cells (SOFC) and solid oxide electrolysis cells (SOEC) are promising technologies which are gaining importance in today's rapidly developing energy frameworks. In particular these high temperature variants offer further potential benefits such as increased fuel flexibility and higher system efficiencies. One of the significant challenges for SOFCs is the creation of robust, durable and affordable cells. While the search for new materials remains an important research activity the role of process development for fabrication and manufacture should not be underestimated. Indeed better understanding between materials, processing and the resulting microstructure is vital for improving cell performance. The links between cell design and various processing techniques are explored. The most common approaches are based on thick film ceramic processes where recent trends include areas such as production of thinner tape cast layers and challenges in the application of aqueous systems to cell processing. Decoupling the processing and control of bulk and catalytic microstructures within the cell has recently been a very active area of development with techniques such as impregnation and exsolution showing increasingly promising results. Thin film techniques such as PVD are also still being investigated for micro-SOFC or thin interfacial layers. In all cases materials and process development should be closely linked, as high quality, reliable microstructures are essential to optimise the chemistry taking place on the materials and viable routes to manufacture are vital to transferring new materials into commercial devices.

SOLID OXIDE ELECTROCHEMICAL CELLS

Electrochemical devices, such as fuel cells and electrolyzers are a promising range of technologies which are gaining importance in today's rapidly developing energy frameworks. As they utilise direct electrochemical conversion between chemical and electrical energy they avoid many of the thermal limitations (such as Carnot cycle) and offer the possibility of high conversion and system efficiencies. These devices generally consist of two porous electrodes separated by a dense electrolyte and are generally classified by the type of electrolyte used. This electrolyte, due to the related conductivity and stability aspects also defines an operational temperature range. This review focuses on solid oxide fuel cells (SOFC) or solid oxide electrolyzers (SOEC) where the electrolyte is based on a solid oxide, most commonly a yttria stabilised zirconia (YSZ), however gadolinia doped ceria (GDC) and strontium doped lanthanum gallate (LSGM) have also been used. These oxides are oxide ion conductors and depending on the type of electrolyte used and the cell design operation temperatures can range from 500°C to 1000°C.
The general principle of operation of the SOFC is shown in Figure 1 where a fuel is oxidised on the anode, liberating electrons. These can be routed round the external circuit to perform work before combining with oxygen from the air to form an oxide ion. This ion can then diffuse across the electrolyte to combine with the fuel to complete circuit. The simplest reaction is shown with hydrogen and oxygen with water as the product, giving rise to the term hydrogen fuel cell. However with SOFC this term is quite a misnomer as the higher temperature of reaction allows the utilisation of a far wider range of fuels such as natural gas, biogas, methane, CO, natural gas, methane and other hydrocarbons such as LPG and diesel. The principle of operation of the SOEC is basically the reverse of the SOFC, shown in Figure 1, where in the simplest cases the cell can be driven with an electrical current to split water into hydrogen and oxygen, with the oxide ions being driven across to the oxygen side of the cell. Again the higher operating temperature of the cell leads to some advantages such as a reduced electrical demand on the electrolysis leading to higher conversion efficiencies over lower temperature devices. Other compounds can also be electrolysed, of significant interest at the moment is carbon dioxide, especially when mixed with steam. The electrolysed output of this is a combination of hydrogen and CO, synthesis gas, which can then form the basis for liquid hydrocarbon production via processes such as Fischer-Tropsch. Other systems are also being developed that are based on proton conducting electrolytes such as BaZrCe oxides or other perovskite materials which are showing promise for the carbon free synthesis of high value chemicals such as ammonia. As the devices materials and process are similar between the SOFC and SOEC (indeed the same device may be used reversibly) in this text we will use SOFC as the terminology, however techniques discussed are applicable to both.

Many reviews of solid oxide devices tend to concentrate on the materials themselves and there are many fine examples available. Therefore in this review the focus will be on the process techniques themselves rather than the materials used. While materials are an extremely important part of the overall picture, the cell performance is governed by both the composition and the microstructure of the material, both of which interact strongly with the processing. While microstructure is obviously a result of the physical and thermal history of the material, the chemical composition may dictate or limit potential processing routes.

CELL DESIGN

Within SOFC technology, subgenres are generally classified by geometry such as planar, or tubular, with the support mechanism acting as a further sub-classification, in the case of planar this can be anode, electrolyte, cathode or metal supported. Each of these geometries carry their own advantages and disadvantages, such as mechanical robustness, but tricky current collection in tubular systems and ease of manufacture, but sensitivity to thermal and mechanical stresses in planar.
In all cases the devices consist of multi-layer ceramic structures and the processing is controlled to create these with the required microstructures in the correct place whether these are porous layers, dense layers or a mixture of both. The actual thickness of each of the layers depends both on its function and the cell geometry and fall across as spectrum from submicron to close to 1mm. Layers required for structural support will of course be at the thicker end of the spectrum. In an electrolyte supported cell the supporting membrane will typically between 150-300μm thick. The thickness has to be balanced between providing enough strength to provide the structural integrity required to support the cell while at the same time minimising the ohmic resistance across the membrane. The need to reduce cell operating temperatures has pushed the requirement to reduce ohmic resistance further, requiring higher conductivity materials such as scandia doped zirconia in supported systems\textsuperscript{15}, or an electrolyte thickness below that suitable for structural integrity\textsuperscript{16}. This latter approach resulted in the prevalence of electrode (mostly anode) supported cells as the most common geometry currently under development, the main variants of which are shown schematically in Figure 2.\textsuperscript{17, 18} Cathode supported cells have been investigated, however the better mechanical properties of the Ni/YSZ anode cermet have led to this becoming the prevalent support. Cathode supports found more favour in tubular devices, most notably the large Siemens Westinghouse tubes where the improved mechanics of the tube mitigate the reduced robustness of the cathode materials.

In the electrode supported cell this element may be 250-1000μm thick, although the trend will be towards the lower end to minimise the effects of diffusion losses in the transport of reactants and products through the porous matrix of the electrode\textsuperscript{19}. In this case the electrolyte may range from submicron to a few 10’s of microns in thickness, with 5 to 15μm probably being the most common range. As well as the main support, other thinner (5-15μm) electrode layers optimised for electrochemistry may be situated between the support and the electrolyte\textsuperscript{20, 21}

A further development of the anode supported cell has been the metal supported cell. Targeted at the intermediate temperature range of 500-750 °C with GDC electrolytes utilised for temperatures below 600 °C and thin YSZ layers for the higher temperatures. In this concept the support is transferred from the ceramic components to a porous metal structure which will act both as a robust support but also a high conductivity current collector with thin ceramic membranes on top. This offers the prospect of reduced materials costs, especially if common engineering alloys such as ferritic stainless steel or Hasteloy can be utilised, along with improved robustness and ease of manufacture via welded cell components. Both tubular and planar geometries have been proposed with the latter being more common.\textsuperscript{22, 23}

One of the biggest challenges in metal supported cells is avoiding oxidation of the support during the ceramic processing phases. Physical vapour deposition techniques, such as vacuum plasma spraying, have been trialled to put down ceramic layers directly onto supports and avoiding any high
temperature sintering stages. Other routes have used tape casting and screen printing to form supporting and active layers respectively, however this often results in the need of a firing step in a reducing environment adding both cost and complexity to the processing. In an attempt to separate the processing of support and catalyst functions and simplify processing infiltration of catalysts onto preformed supports has been investigated. This is similar to that discussed later in this review, allowing lower temperature formation of the desired catalyst phases. In addition to these processing challenges, metal supported cells can also be susceptible to inter diffusion of catalyst and support structures during operation leading to degradation, with investigation of potential solutions to these issues an important area of work.

Tubular cells were the first significant iteration of SOFC scale up with the large Siemens Westinghouse tubes in the late 1980’s and 90’s with tube lengths of the order of 2 metres and designed for larger pressurised systems in the 100’s kW range, shown in Figure 3a. Although over intervening years planar systems have become the most common design due to the potential for high volumetric power densities in stacks, there has been continued development effort in tubular. This has been particularly manifested in micro-tubular where tube diameters are a few mm to cm and lengths are generally a few cm to 10’s cm rather than the metres length scale of the early Siemens Westinghouse designs (Figure 3b). These micro-tubes are generally well suited to smaller systems from a few Watts to a few hundred Watts.

One of the advantages of the microtubular cell is the mechanical robustness afforded by the tube. This allows for fast thermal cycling and redox tolerance. This mechanical advantage also allows for the consideration of cathode supported designs in addition to anode and electrolyte supports. The supporting element is often extruded. This can be room temperature extrusion of a viscous ceramic paste. Here the ceramic is deagglomerated and mixed with binders and solvents before extrusion, the solvent systems can be organic solvent or aqueous based systems. The extrusion process itself can be batch based ram extrusion or a continuous process based on transport of the paste along an Archimedean screw, the latter process having obvious attractions for an industrially focussed process. As well as the cold paste viscous plastic process (VPP) type extrusion, work has also been carried out to investigate the use of thermoplastic processing. Here the ceramic is dispersed within a molten polymer matrix, such as polypropylene, which once cool results in a solid room temperature structure. The polymer is burnt out during the sintering phase resulting with the final fired ceramic body. Other layers are often deposited by slurry techniques such as dip coating, spraying or slip casting however co-extrusion of multiple layers has also been investigated as a method of producing the complete cell in a single process.

For all of the mechanical advantages, tubular cells still suffer from difficulty in current collection, especially from the inner surfaces of the tube. This has resulted in a number of potential design
solutions from cells connected end to end or wires or other conductors projecting from tube ends. Clusters or blocks of cells have also been proposed, however in some of the more complex designs parasitic currents between adjacent cells must be a potential issue. No definitive design solution to this issue has been proposed or revealed in which the difficulties of current collection in a tubular system has been elegantly solved. However this area remains a busy segment of research and a number of review articles cover the developments in far greater detail that is possible here.

There have been some geometries which have attempted to combine the positive attributes of both tubular and planar, while avoiding the negatives of both approaches. These tend to be hybrid type designs where standard thick film processing routes of the planar concepts can be incorporated into a tubular system. As illustrated in Figure 4 these can be attained either by applying cell arrays to a flat sided presintered support tube as in the segmented in plane design. Or by tape casting and screen printing flexible green layers in a planar arrangement before rolling into a double spiral to gain the mechanical benefits of the tube on the SOFCRoll concept.

THICK FILM PROCESSING

For the popular planar designs it can be seen that many of the layer thicknesses favour the use of thick film process techniques which provides a good match of the required film thicknesses with that of the thick film process output (a ceramic thick film nominally being defined between 5 and 500 microns). These have become the widest of the ceramic processing techniques employed in the production of SOFC and of these, tape casting and screen printing have become prevalent. Using these two techniques it is possible to cover most of the common layer thicknesses used in SOFC with screen printing covering the lower end from 5-50 microns and tape casting the higher end up to 500 microns and beyond. The relative popularity of these particular processes is due not only to the thickness matching, they also meet many of the requirements for adoption by mass manufacture to be discussed later and this is highlighted by the wide spread use of both techniques in the hybrid electronics industry where they are used to manufacture large numbers of complex multilayer components on a commercial scale for decades. Finally the nature of the processes allows for the introduction of new materials and for slurry characteristics to be engineered resulting in specific microstructures.

Other slurry based processes have also been applied to SOFC such as ink jet printing, dip coating, spaying, spin coating and while they have produced effective results they have not quite found the same wide spread penetration of screen printing and tape casting. This could be due to a
number of factors such as slower deposition times or the need for inherently batch based production. However in specific circumstances their application can be advantageous, such as in the coating of uneven or curved surfaces. Other techniques such as roll coating have also been trialled and have produced promising results. These may be most suitable for larger area coatings where techniques such as screen printing become unwieldy.

The basis of all these processes is the creation of a stable slurry or suspension, where ceramic particles are well dispersed into a liquid phase. This will often be a mixture of solvents and polymers, matched to give the correct rheological, drying and unfired “green” behaviour. There may also be other constituents of the slurry such as plasticisers or pore formers the presence of which may be required for green properties such as flexibility, surface tack for laminating or specific fired microstructures.

**Trends in Tape Casting**

While the tape casting process itself is well established in SOFC manufacture the technology continues to evolve with new directions and trends. One of these is recent work to push the thickness of the cast layer to ever thinner values. Tape casting is often regarded as a means to produce thicker layers between 100μm and 1mm. However there have been several reports recently of tape cast electrolytes below 50μm and even down towards 10μm. At these thicknesses however the electrolyte must be supported and an unfired cast layer often laminated onto a thicker supporting tape cast anode support before cofiring. From this further developments have progressed into sequential casting, where the removal of any lamination processes and promotion of good interfacial bonding are significant process advantages. Here an initial layer is cast and dried, the doctor blade is then adjusted and the tape rewound back under the casting head. The subsequent layer is then cast directly onto the initial dried layer. In these layers the thin electrolyte layer is often cast first, however thicker support layers can also be cast first and multilayer structures can be built up as shown in Figure 5 which are of promise for infiltrated catalyst structures discussed later. The next development of this approach will be the move to demonstrating true co-casting where multiple layers are cast simultaneously, although often discussed it is rarely demonstrated with only a few examples in related applications.

Casting thinner layers presents several processing challenges. Any effects of thickness variation or poor dispersion can be exaggerated and the thinner layer also requires smaller particles which can exacerbate dispersion issues. A single agglomerate that may result in a non-critical defect in a thicker tape can lead to a physical breach in a thin tape which, for example, is for an electrolyte membrane may result in gas leakage across the cell. The thin tape may also have weaker mechanical properties than its thicker relative and so higher levels of binder and associated organics are often required, this can result in higher levels of shrinkage on drying and firing. This can be particularly troublesome
in cofiring environments as it is important that shrinkages are matched with thicker tapes. These requirements tend to lead to a general condition where slurries for thin tapes are lower in viscosity and cast at a higher speed than thicker counter parts. A final challenge may be the limits of the casting equipment itself with very thin casting gaps approaching the tolerance limits of more basic casting equipment, such as flatness variations across the width of a doctor blade or granite casting block.

**Aqueous Thick Film Processing**

Due to their stable, predictable behaviour non-polar organic solvent systems have gained a strong position in SOFC processing. However there are ongoing concerns with their continued use. These are due to environmental concerns through emissions, health and safety for both prolonged worker exposure and fire or explosive risk. Mitigating for these add complexity and cost to process infrastructure while potential legislation could make future availability problematic. Therefore there has been increased interest in water based systems as a potential basis for future processing. While not in itself a new technique, aqueous systems have been used in certain ceramic industrial processes for a significant time, it has not been so widespread in the SOFC industry where the stability of non-polar systems have been favoured.

In more polar and aqueous based systems the electrostatic interaction of the particle and solvent system become much more important. This interaction is measured via the zeta potential which is the magnitude of the particle surface charge in relation to that of the solution in which it is suspended. If the value of the zeta potential is large (either positive or negative) then this will result in a strong interaction with counter ions and produce an electrically repulsive double layer around the particle. This prevents particle coming close enough together for attractive Van der Waals forces to dominate and a stable well dispersed solution will result. Where the zeta potential is small (< ±20-30mV) the repulsive forces are reduced and Van der Waals forces will dominate leading to flocculation of the particles. The zeta potential is heavily influenced by pH which can be dynamic within a system, also further influence can arise from different powder chemistries and even preparation differences in powder with nominally the same chemistry. The chemical interaction between water and certain ceramic surfaces can also be far more pronounced than in non-polar systems, in particular materials susceptible to hydrolysis; such as CaO and MgO (SOFC specific materials in this category can include many common cathode materials such as LaSrMn oxides (LSM)) may be difficult to work with in water based slurries without more complex powder preparation. This leads to a far more complex picture which is less tolerant to minor processing and environmental fluctuations as well variations between powder batches.

Where purely electrostatic repulsion is not sufficient to maintain a stable suspension, dispersants can again be used to prevent flocculation. In a polar system these will often work via an electosteric...
mechanism where the electrical dipoles in the dispersant tail help promote the electrical double layer, with the length of the chain also contributing to some steric dispersion effects. As mentioned above dispersants are usually formed from an anchoring head with a tail that will extend out into the solvent. They are classified by the charge on the head group and can be cationic (+ve), anionic (-ve) or non-ionic, where there is no direct electrical charge but the head will have a polar group leading to a diploe effect, use will depend on the both the nature of the particle surface and the free ionic species in the solution.

The rheological behaviour of aqueous slurries is also closely linked with pH. The lowest viscosity in a concentrated dispersion is usually seen when all of the individual particles are well dispersed and these effects can be seen as zeta potential varies with pH. Minimal viscosities will be observed where zeta potentials are strongest, usually high or low pH's. Where zeta potential is weak and there is a propensity for flocculation viscosity will be higher.\(^7\) This is due to trapping of solvent molecules in between agglomerated particles so effectively removing them from the solvent body. Capillary mechanisms present in non-polar systems also play a part in aqueous systems, however these can be exacerbated by the electrical dipole on the water molecule acting as another source of attraction and entrapment.\(^7\) The polar nature of aqueous systems also leads to interaction between particle surface charge, the electrical dipoles on molecular side groups on binder polymer chains and other constituents in the slurry formulation. The long chain polymeric nature of these molecules can lead to formation of long range structure within the slurry. This may be due to attraction, such as hydrogen bonding, between the polymer chains themselves, the polymers and particles or other molecules in the solution.\(^7\) Formation and subsequent breakdown under conditions of shear of this loose structure can lead to yield and non-Newtonian flow behaviours, such as pseudoplasticity and thixotropy.\(^7\) While some pseudoplasticity is welcome too much thixotropy can be troublesome due to poor edge and thickness retention in a cast layer. Study and investigation the fundamental characteristics of this interaction form a significant part of the work into improving the understanding of these systems.\(^7\)

Another important consideration in aqueous systems is the higher surface energy and tension. This has several implications for processing, not least matching of these when creating multi layer systems. Multi layer fabrication and printing onto green substrates is well practiced throughout the industry.\(^7\) If the surface energy of the substrate and the surface tension in the deposited slurry are not well matched (such as printing a high surface tension water based ink onto a low surface energy non-polar tape) then dewetting will occur leading to poor coverage of the deposited layer. It is therefore best to have similar solvent systems throughout the processing procedure and avoid mixing polar and non-polar. This would therefore demand that all slurry aspects of the process were changed at a single time rather than allowing more incremental change. This would rightly be viewed as a high risk operation and in concert with the higher sensitivity of aqueous systems, demonstrates why the conversion from established non-polar systems to aqueous systems is somewhat limited in industrial settings.
Another aspect of the higher surface tension in aqueous systems is the ability for stable bubble formation. 78 This has the most significant impact during milling where significant foaming can be observed. Other potential effects can be bubble formation in the deposited layer, such as in screen printing after screen separation, resulting in pin holes or other flaws promoting crack propagation during firing. 79 While in many cases foaming and bubbles can be avoided by addition of antifoaming agents (often surfactant type molecules which alter the surface tension) or careful control of process parameters they demonstrate an increase in the complexity or sensitivity of these systems over their non-polar equivalents. Although in certain circumstances the formation of stable foams could be considered advantageous for the formation of specific microstructures.80 This microstructural engineering advantage is further extended due the far larger range of polymeric based materials that can be considered as pore formers due to their immiscibility in water. This gives an increased range pore morphologies which can be easily created and will be discussed in the following section.

**Bulk Microstructural Control**

The performance of SOFCs has a close link to the microstructure of the various layers of which it comprises. In particular the porous electrode layers have significant effect with fine grains and porosity being favoured close to electrolyte interfaces so that the high surface area provides a large triple phase boundary thereby minimising polarisation losses in the electrochemical reactions. This is further enhanced by the use of composite structures where inclusion of electrolyte materials in the electrode structure extend theses boundaries further. Further out from the electrochemical interface mass transport of reactants and products and minimising of electrical resistance across necks between particles leads to the requirement for a coarser structure composed of larger particles with more open porosity. These differing requirements within the electrode led to the development of layered structures, often these would consist of a fine inner electrode structure and thicker outer current collecting layer comprising the coarser structure. In some cases multiple layers were deposited by screen printing or similar methods in so that they varied either compositionally, structurally or both from the previous layer so aiming for a more gradual progression between the structural needs of the electrode and the current collector, that aim being to minimise any mechanical stress from a sharp transition between the differing microstructures of the electrode and the current collector. 81 The ultimate aim here would be a fully graded structure with a smooth continuous transition between a fine inner and coarse outer structure, a number of approaches have been tried with the progressive dendritic structures of the freeze casting technique, shown in Figure 6, looking particularly interesting.82 83

Figure 6; SEM Cross section of SOFC fabricated with a freeze tape case NiO/YSZ support showing the specific microstructure arising from this technique, scale bar 100μm [Ref. 82]
The simplest approach to microstructural control comes from control and manipulation of the particle size distribution of the powders themselves along with the sintering temperature. Larger particles have slower sintering kinetics and often result in large residual porosity, whereas smaller particles will form a network of finer porosity well suited to good electrochemistry. Therefore with careful control of particle size distribution by calcination and milling the sintering and hence the morphology of the porosity can be controlled at a given temperature. This can be further tuned by varying the sintering temperature to either push or retard the coarsening and densification processes. In the case of Ni based anode materials further porosity is introduced as the NiO reduces to metallic Ni.

These basic approaches are useful as they do not require further additions to the slip formulation and so minimise complexity and to some extent costs. However there are times where this manipulation will not be able to produce the balance of porosity, ceramic network and surface area required and in these cases further additions in the form of pore formers must be utilised. In most of these cases the pore former is a fugitive phase that burns out during the firing stage. Common pore formers are carbon blacks, graphite and rice starch. These are commonly used in the polar organic slurries common in SOFC fabrication as they are insoluble in these systems. In general the shape of the pore will be influenced by the pore former with this acting as a template for the pore. In cases where there is a strong anisotropy in the pore former, such as the platelet form of graphite, Figure 7, care must be taken to ensure any orientation during processing does not adversely affect the functionality of the pores. Another important consideration is the temperature at which the pore formers burn out from the green structure. With organic polymer based materials this is likely to be around 150-300°C depending on the nature of the polymer used. With carbon based materials such as graphite it will be much higher, around 800°C. While strong templating to the pore former is seen in both cases there is may be differences in the way the ceramic matures around this as there may already be some ceramic necks forming at the higher temperature whereas at lower temperatures the loosely bonded structure will have for more opportunity for movement and shrinkage as the temperature increases and the ceramic begins to consolidate.

While much of the early work concentrated on porosity development within bulk electrode materials such as LSM or Ni/YSZ cerments, recent developments towards infiltrated catalyst structures deposited onto supporting skeletons (described later) has put an increased emphasis on the control and engineering of porosity within these. Therefore maximising the potential range of pore formers is an important consideration and in concert with the health, safety and environmental aspects described above this has pushed interest towards aqueous processing as a route to create a wider range of pore morphologies, example of which are shown in Figure 8. Utilisation of aqueous systems opens up a wider range of materials for use as pore formers such as polystyrene (PS) and polymethyl methacrylate (PMMA) which although have been trialled in nonpolar solvent based systems are generally soluble in these which is detrimental to the templating aspect of the pore.
former particle. These materials are available over a wide range of controlled sizes from single micron values to 10’s micron scale so cover the range of pore sizes advantageous for SOFC electrode structures. As well as polymer materials other approaches have included use of emulsion droplets and carbon spheres synthesised from pyrolysis of sugars. An advantage of the latter approach is the higher decomposition temperature of the carbon gives some advantages similar to using graphitic materials but without some of the morphological limitations that come from the platelet form of graphite.

Many examples of improved electrode performance using varying combinations of pore former exist. However there are so many variables between the specific process routes that it is difficult to draw meaningful conclusions over the whole field. However it is often obvious that within any system there will be a optimum performance point where the maximum benefits of the microstructure are realised. This varies depending on the specific system and is linked not only to the pore former but also the ratios of other components of the system such as binders and plasticisers. This has been driving the growth of advanced characterisation techniques to better quantify the attributes of these complex structures and deconvolute the important aspects governing performance so leading to future improved design. In addition to templating methods other methods such as foams, blown films and reticulated structures are being considered for the manufacture of highly porous structures such as cellular structures, where pore volume is to be maximised with minimum solid fraction of ceramic.

**Catalyst Infiltration**

It has now become recognised that control of the electrochemical interface is a significant aspect of creating high performance cells and one of the most significant trends in SOFC fabrication over the last few years has been the emergence of control of the morphology of this interface by either by catalyst impregnation or exsolution with the general variations of these being illustrated in Figure 9.

For infiltration, catalyst precursors, often in the form of nitrate solutions, are loaded into a porous support skeleton before thermal processing to decompose the precursor solution and result in the desired catalyst phase being supported on the skeleton. The microstructural engineering of these skeletons, described above, is an important part of this technique as the separation of the thermal processing of skeleton and the catalyst allow for both to be tailored, optimising their individual functionalities and avoiding the compromises often required in the processing of multi-phase systems.
Much of the early work on infiltration was based on anode materials where appropriate solutions of the copper nitrates were investigated for the in-situ formation of Cu catalyst on porous YSZ scaffolds. This had advantages of avoiding the high temperature ceramic processing steps required to form the ceramic phase and allowed the application of materials such as copper whose melting points would be beyond the ceramic processing temperatures. Also the lower processing temperatures resulted in finer catalyst structures, which when combined with an oxide ion conducting YSZ support scaffold offered the opportunity for high triple phase boundary regions and subsequent electrochemical high performance. Similar performance enhancements have also been seen for impregnation of percolating Ni catalyst, especially when combined with ceria addition, providing both better polarisation resistance and improved carbon tolerance.

Promising work has also been carried out on infiltration of oxide based fuel catalysts and this has proved to be a promising method for the introduction of non-nickel oxide based catalysts. Again based around perovskite materials such as LaSrCrMn (LSCM) or LaSrTi (LST) oxides, they offer a number of advantages over more traditional Ni based cermets such as reduced sensitivity to redox cycling, increased resistance to coking from carbonaceous fuels and potentially improved sulphur tolerance. This offers the prospect of far more robust anode systems with advantages of simpler, therefore less expensive, system design and increased fuel flexibility. Further details on the chemistry, synthesis and infiltration can be found in more materials based reviews and papers.

In terms of processing the finer structures offered by infiltrated routes has proved advantageous in the attainment of improved performances bringing these materials towards practical application in realistic systems.

Although redox stable, infiltrated LSCM materials show interesting behaviour when cycling between oxidising and reducing environments. After heat treating of the precursors in air a smooth continuous coating of the LSCM perovskite is formed on the surface of a supporting yttria stabilised zirconia skeleton. However once exposed to reducing atmospheres a morphological change is observed with the coating appearing to de-wet with the formation of nanoparticles on the surface of the support the effect of which is shown in Figure 10. This effect is linked to the transition of the Mn cation between the 3+ and 2+ oxidation states and the changes in solubility these in the zirconia skeleton. This produces a catalytic surface with a high surface area beneficial for the electrochemical reactions.

In LST based systems, while some work has been investigated impregnating these onto YSZ or CGO support skeletons much of the promising work has been carried out using the LST as the support skeleton with further electrocatalyst impregnation. When reduced LST based skeletons can exhibit adequate conductivity, around 28-30Scm⁻¹, which when combined intelligently in a two layer anode structure which separates electrochemical and current collection functions is sufficient for efficient SOFC operation. The LST material has good structural stability during redox and shows good
cycleability in the conductivity behaviour. The LST also shows good chemical compatibility with standard SOFC electrolytes such as stabilized zirconias and permits processing using cofiring routes for both electrolyte and anode supported systems.

Common catalyst impregnates for LST systems have been nickel and gadolinia doped ceria. A number of ratios between the two have been investigated along with varying infiltration sequence. Where the ceria phase is impregnated and heat treated before the infiltration of the nickel a near continuous coating of the ceria phase is observed with nano particle of nickel in the surface or embedded into this. In a SOFC anode environment this will result in a very active surface with both the partially reduced ceria and metallic nickel actively contributing to the fuel oxidation. All have so far shown promising results and optimisation of precise sequences and heat treatments to maximise performance and enhance durability remain a highly active topic of research.

The potential for scale up of the LST has recently been demonstrated with the application of infiltrated LST anodes of a Hexis 1kW class Gallileo system. Cells all comprised a 10% A-site deficient La$_{0.20}$Sr$_{0.25}$Ca$_{0.45}$TiO$_3$ (LSCT) anode skeleton, where the addition of the calcium helps enhance the sinterability so allowing formation of well bonded ceramic grain while maintaining the open porosity required of an anode microstructure. Infiltrated catalysts were a mixture of 10wt% gadolinia doped ceria and 5wt% nickel. Figure 11 shows the initial performance of this system was around 0.75kW and was very encouraging for a new anode system at this level. However the degradation was worse than that observed both at single cell and short stack level and was attributed to less precise temperature control leading to hot spots in the stack and subsequent growth and coarsening of the catalyst particles.

However this scale up exercise also revealed a number of potential challenges that remain to be addressed with infiltrated catalyst systems. Firstly, the process of infiltration itself can be rather slow and cumbersome with a number of sequential treatments required to build up the desired catalyst loading. This is one area where ink jet printing may find itself a very useful technique providing a controllable and scalable technique to apply sequential treatments of nitrate solutions. Also while in the form of the nitrate solution the catalyst will be drawn through any porous body by capillary action. While this is not an issue on a larger area planar single cell, it could prohibit application of the technique to more complex geometries such as segmented in series designs where a number of cells are supported on a generic porous support and it is designs such as this, comprising of cells made up from thinner multiple layers of current collector and electrochemical functions that the ceramic based anode materials could potentially be employed.

In order to capitalise on the observed advantages of the infiltrated microstructures a number of alternate approaches are currently under investigation. One is to precoat the support particle with the required nitrate solution and heat treat this to a temperature just sufficient to decompose the
nitrate but not coarsen the primary particle. This can then be processed by all the conventional ceramic routes such as tape casting or screen printing and then when exposed to reducing atmospheres in the anode chamber reduction produces nanometric catalyst phases on the surface. This avoids the issues of capillary action mentioned above, however as this often involves lower catalyst loading is best employed with a conducting backbone such as LSCM or LSCT.

Infiltration has also been applied to cathode manufacture, again mixed precursors, often mixed nitrates of La Sr and Mn are introduced to the porous skeleton with the perovskite phase forming on heat treatment. As with anode structures the low temperature formation leads to a fine structure with high surface area and good performance. The low temperature of perovskite formation was also attractive for the formation of more electrochemically active materials based on lanthanum cobaltites, such as LSC and LSCF. These mixed conductors possessed excellent performance for the oxygen reduction reaction and high levels of electrical conductivity, however their widespread adoption had been plagued by issues surrounding rapid formation of zirconate and a mismatch of coefficient of thermal expansion which resulted in extremely problematic traditional ceramic processing with zirconia based electrolytes. Some of this work has shown some encouraging results and research continues to optimise stable structures for long term operation.

Surface Exsolved Structures

One question that was often asked during the development of the surface coated or infiltrated anode structures was what was the nature of the interaction between the infiltrated phase after heat treatment but before reduction? Did this remain as a surface coating or was there some dissolution and interaction with the underlying support? This was more evident in the precoating of powder where the lower levels of nitrate used could potentially result in surface enriched core-shell type structures on the base particles, rather than a well defined coating. This had potential implications both for cycling of the structure and more importantly pinning of any exsolved or precipitated phase to the lattice to prevent coarsening.

This lead to investigation of a new doped perovskite family where the stoichiometry is deliberately manipulated to give a single phase during processing in air but exsloving metal catalyst particles when exposed to reducing atmospheres. This is a potentially very elegant solution to a number of the challenges faced by infiltration techniques allowing a single phase material to be handled throughout the processing stages but resulting in the desired fine catalyst structure when in operation.

Strontium titanates are currently receiving much attention as the basis for exsolved structures. Here A-site deficient stoichiometries are created with the desired catalyst species doped onto the B-site. When exposed to reducing atmospheres there is a drive to form a local ABO₃ lattice structure in concert with the generation of oxygen vacancies, which forces the doped catalyst phase on to the...
surface as a nanoparticle as shown in Figure 12. A wide range of nanoparticles can be exsolved with research including Ni, Pt, Pd, Ru and Rh and optimisation of various compositions is an active area or research.

The anticipated interaction with the base ceramic has been observed with pitting revealed under exsolved particles (Figure 13). This effectively pins the particle to the base ceramic and as well as preventing movement and coarsening of the catalyst particles it has been shown to improve resistance to damage through carbon deposition through the pinning preventing damaging Ni detachment during growth of carbon whiskers.

From a processing and manufacturing perspective the significant advantage of this approach is the fact that in air the ceramic remains a stable, single phase oxide material. This allows processing in air utilising conventional techniques such as tape casting and screen printing and avoids complex firing schedules in controlled atmospheres. This maintains the cost effectiveness of the processes and allows for straightforward integration of the new materials into existing manufacturing protocols, an important attribute for any new material.

**THIN FILM PROCESSING**

In this context thin films are described as being of the order of 1μm or below. Although in certain cases they may be slightly thicker with some overlap to the lower end of thick film processing. Thin films are generally processed via chemical or physical vapour deposition routes, although other techniques such as sol-gel and spin coating have also been investigated. However CVD and PVD techniques have the ability to deposit high quality dense ceramic thin films without the need for further sintering or heat treatment. Thin films have obvious attraction for electrolyte deposition, especially in reducing the ohmic losses across materials such as 8YSZ. A major exponent of these techniques was Westinghouse (later Siemens Westinghouse) who used electrochemical vapour deposition to deposit electrolytes onto their tubular cells during the 1980’s and 1990’s. However after considerable development and scale up it was eventually conceded that the costs inherent in the processes could not be significantly reduced and that scale up would also not effect a large enough cost reduction to allow the technology to compete with other generation methods. Therefore the approach was abandoned. This somewhat tainted these technologies as uneconomical for SOFC applications however there has been a recent resurgence of interest in thin films both for the production of micro-SOFC and the deposition of thin barrier layers.
Micro SOFC

Micro SOFC take miniaturisation to the extreme and are aimed as an alternative to Li ion batteries in small electrical devices with power outputs in the range of 1-20W. SOFC’s in this role have a number of potential advantages they can be operated on high energy density fuels such as butane and propane which have long been readily available in small portable volumes, secondly the devices offer high specific energy density, higher even than Li ion or Ni metal hydride types secondary batteries so minimising size in portable devices.

As these cells are planned to operate within already small devices the micro aspect must not only be carried to the cell but also the other infrastructure such as thermal insulation etc. This means that operating temperatures must be well within the intermediate temperature range of below 650 °C, even down to 350 °C. Cell membranes must therefore be extremely thin, below 1 µm and towards a few 100 nm’s. To achieve this membranes utilise micro-electro-mechanical system (MEMS) microfabrication techniques common in the semiconductor industry. Here small free standing membranes are deposited onto various types of silicon, glass ceramic or nickel substrates where they either bridge perforations or have the substrate etched from underneath with a number of designs and concepts being pursued an example of which is shown in Figure 1.

However a number of technical issues remain to be overcome mainly in terms of membrane integrity, and system integration issues. Assuming these issues can be overcome, there is still the issue of cost inherent in a number of the processes involved in the fabrication. However in this case the high specific energy densities of micro-SOFCs coupled with the ability to rapidly change a small fuel canister could provide a distinct advantage over other energy technologies. As portable electronic become ever more power hungry and consumers less willing to be tied down while recharging this might be an advantage that people will pay for in what must be remembered are already high cost devices already containing components using similar fabrication techniques.

Inter Layers

The use of interlayers, usually between electrolyte and electrodes has become a common approach in the development of high performance cells. These layers will often protect a YSZ electrolyte from formation of deleterious phases from high performance but highly reactive cathodes such as those based around Sr doped lanthanum cobaltites and ferrites, or to prevent electronic leakage in GDC electrolytes by the application of a thin blocking layer of YSZ. In both cases this layer will contribute to additional ohmic resistance and so the thinner this can be made the better. Recently there have been a number of investigations looking at the application of PVD films in this role. Some very fine and dense films have been produced, such as the one shown in Figure 15 and good performances and reductions in degradation have been observed. However in these cases the question of process cost is extremely relevant, specifically are any extra costs justified and vindicated by the
performance improvements observed. With this question in mind some efforts have looked to use colloidal and sol-gel techniques to achieve similar goals using routes requiring less capital intensive equipment.\textsuperscript{132, 133} Although very promising these routes then introduce potential issues of drying and sintering and the introduction of cracks and flaws in the film during these operations and careful control of both substrates and process protocols are required.\textsuperscript{134}

**FIRING AND SINTERING**

When using particulate or slurry based ceramic processing methods at some point the green object must be subjected to a high temperature firing step to burn out organic carriers and allow the ceramic particles to coalesce and sinter into the final desired microstructure. As described above a number of the layers in the SOFC may be prepared together in the green state and co-fired together. This has a number of advantages such as promoting good interfacial bonding and minimising the number of high temperature firing required to produce the final device, especially important in minimising costs.

However the co-firing process can introduce further complexities to the processing, in particular if layer shrinkages are mismatched. A lot is discussed about the need to match coefficients of thermal expansion (CTE) in multilayer devices and while this is important for thermal cycling of operational devices, of more significant importance during the manufacturing stages is the shrinkage due to removal of organic binders and then the sintering of the ceramic particles themselves. As the binder burns out the body goes through a number of stages, firstly a very fragile, biscuit stage where binders have gone but particles have yet to coalesce and a more viscous phase where particles are moving in the sintering processes. Where these movements are mismatched warping delamination or cracking will occur. Application of flattening loads can minimise this, however if these are not optimised then fracture will occur if the load is too heavy, due to constraint of movement during the early stages of firing when the ceramic is still very fragile or warping will still occur if too light.\textsuperscript{135} Alternative methods being investigated include changing the ratio of coarse and fine particles in layers to promote particle rearrangement, especially during debinding stages, and it has been shown that with careful control in each of the layers warping can be minimised.\textsuperscript{136} Similar effects are seen with nanoscale powders where rearrangement in low stress environments can produce denser final bodies than pieces with higher green density but high internal stress.\textsuperscript{137} The interplay between the layers is a complex interaction and modelling this remains an important aspect of gaining improved understanding into the mechanisms at work.\textsuperscript{138}

When layers are fired on a prefired substrate this can prevent shrinkage or constrain movement and so result in cracking, residual porosity, excessive grain growth or delamination.\textsuperscript{139} In these circumstances the drying and sintering needs to allow for adequate reorganisation of particles to
overcome the constraints applied by the substrate. Similar to co-firing above, careful drying and combination of particles can be used and in some circumstances application of multi-step firing regimes, where temperatures are taken briefly to a higher temperature than the isothermal hold have been shown to be useful in promoting some coarsening and particle re-organisation resulting in reduced porosities.\textsuperscript{140,141}

As the thermal processing steps are considerable contributors to process costs both terms of time and energy required methods or reduce either aspect would be advantageous. Microwave assisted sintering has been receiving attention as a method to increase heat up rates when sintering components and small cells have been demonstrated using this technique.\textsuperscript{142} In a similar vein use of electrical fields in DC assisted flash sintering and spark plasma sintering have also been trialled to reduce both time and temperature of ceramic sintering for SOFC materials. However while promising results have been attained many have been applied to single components rather than full cells.\textsuperscript{143,144,145} Where such techniques have been applied to multiple cell layers they have used on small button type cells with specialist geometries or furnace set ups and the ability to scale up to cells of commercially relevant sizes remains an open question.\textsuperscript{146,147,148} Secondly the requirement for close control of ramp rates in complex multilayer co-fired structures as discussed above structures may ultimately limit application of these sorts of techniques in larger scale cell fabrication.

In addition to firing of actual cells, microwave techniques have been trialled to assist with other thermal processes associated with the processing of SOFC materials such as combustion synthesis of powders, calcinations of raw powders prior to slurry processing and decomposition of nitrates in the infiltration processes.\textsuperscript{149,150,151} It may be in these roles, where simple thermal processes, such a heating to moderate levels, where ramp rates are not critical to success that they find application, in speeding up time consuming processes such as infiltration

\textbf{SOME CONCLUDING THOUGHTS ON SCALE UP AND FUTURE DIRECTIONS}

Any fabrication method that is going to be successful must be capable of scale up. SOFC stacks are made up of many cells and many thousands of units will be required in a fully commercial operation. Therefore any process must be able to achieve high volume production of high performance cells at affordable costs. In addition to the scalability, processes must minimise costs (capital, running and infrastructure), be reproducible, reliable and produce high quality cells. In addition they must minimise environmental impact and exhibit scope for process improvement /development.

This tends to favour the thick film techniques discussed above as they have been proven in demanding cost driven mass production environments and fulfil many of the requirements outlined above. However there are still specific challenges related to SOFC production which may not be surmountable with these technologies and therefore high value techniques, such as PVD may not be completely out of question. Many examples are seen in semiconductor fabrication, however these
relatively expensive processes need to justify investment and costs by bringing significant
performance or production benefits. The revolutionary benefits in terms of new technology and
capability allowed by semiconductor development allowed this value to be realised, new
technologies still tend to be expensive and it is only with time and wider adoption that costs fall, but
often only as the initial technology is superseded by a new more capable iteration.

Unfortunately SOFCs represent a displacement technology rather than a revolutionary technology, in
that many cheap methods of generating electricity already exist that must be pushed aside by SOFC.
Of all the technology areas in which SOFCs are looking to compete, small scale CHP is probably the
most cost sensitive with customers looking for extreme reliability at very aggressive price points.
This is an extremely challenging environment in which to incubate a new technology and work out
the bugs and issues of scale up. It could be argued a better approach would be for SOFC to gain
initial commercial realisation in high value markets where convenience or flexibility are premiums
over cost and reliability this may allow initial costs of scale up and developing reliability to be better
spread and confidence to be gained in the marketplace. As these aspects mature a solid foundation
would be created to build the technology into more commercially challenging areas with a
reasonable chance of success.

Although the focus is often on scale up, mass manufacture and commercialisation, the goal of
developing highly specialised, high cost fabrication techniques with no direct long term routes to
mass manufacture and scale up can still be perfectly valid approaches. In these cases the techniques
can be useful very precise fabrication of a material or experimental device, such as specific
crystallographic design or precise deposition of a patterned electrode, and are of great value in
gaining fundamental understanding of a material or a reaction mechanism within a system. The
knowledge gained here can have a direct impact of the development of improved materials,
processes or operating protocols which can improve the performance, durability and
competitiveness of SOFC devices through an increased understanding of materials, processing and
performance relationships and how these may be optimised.

Research and development in solid oxide fuel cells remains a materials focussed activity and this is
with good reason as there are still significant advances in materials that will be beneficial to SOFC
becoming a commercial reality. However within this activity the role of processing should not be
overlooked. High quality, reliable microstructures are essential to optimise the chemistry taking
place on the materials and viable routes to manufacture are vital to moving these discoveries out of
the lab and into commercial devices, both of these are dominated by processing. Materials and
process development should be closely linked, this will allow rapid identification of synergies
between new materials and processes as well as early identification and solution of potential issues
between materials and processes. This will allow for improved understanding of the practical limits
of differing process techniques and which are the best techniques to be utilised in specific
applications. This will allow practical solutions for many of the technical issues to be developed while
maintaining a view to long term costs and commercial realities.
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References

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Figure captions

Figure 1; Schematic representation of basic SOFC and SOEC operation

Figure 2; Diagram showing the development of anode supported planar cell supports

Figure 3; Tubular cell geometries a) Siemens Westinghouse [Ref.28], b) Micro tubular [Ref.30]

Figure 4; Hybrid cell designs combining planar and tubular aspects a) Segmented In Series SOFC Geometry b) St Andrews SOFC Roll

Figure 5; Microstructure of a Triple layer Co-cast structure with dense YSZ sandwiched between two porous YSZ layers. [Ref. 60]

Figure 6; SEM Cross section of SOFC fabricated with a freeze tape case NiO/YSZ support showing the specific microstructure arising from this technique, scale bar 100μm [Ref. 82]

Figure 7; Effect of pore former morphology on pore shape with plate-like Graphite flakes used beneath the dense layer and a spherical pore former above.

Figure 8; Controlled and engineered porosity using PMMA pore former with carefully controlled pH, pore former volume fraction and surfactant chemistry showing surface morphology at (a) low and (b) high magnification and (c) fracture surface [Ref. 88]

Figure 9; Examples of microstructures evolved from impregnation a) An electron conducting backbone (green) is infiltrated with precursor (orange) which forms dispersed catalyst particles across the surface. This can be a single material or multiple phases. b) An ionic conducting backbone (yellow) is coated with precursors which will form a continuous electron or mixed ion electron conducting perovskite phase (orange). In some cases surface morphology may change with atmosphere to increase triple phase boundary. c) An ionic conducting backbone (yellow) is coated with precursors which will form a network of percolating electronic conducting particles. [Modified from Ref. 102]

Figure 10; Infiltrated LSCM microstructures showing morphology change in differing atmospheres a) from fairly continuous in oxidising (calcination in air at 1200°C) to b) distinct distinct nanoscale grains in reducing atmosphere (5 hours in humidified H₂ (3% water). [Ref. 108]

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Figure 11; Performance data for 1kWe level system with cells running on anodes based LSCT scaffold with infiltrated catalysts (Ni and Ce) a) overall system performance. b) Cell cluster temperatures showing wide variations across the stack with some significantly higher than the average. [Ref. 112]

Figure 12; Electrode microstructure with Ni catalyst species exsolved from bulk skeletal support, the initially A-site deficient, oxygen stoichiometric (La_{0.52}Sr_{0.28})(Ni_{0.06}Ti_{0.94})O_{3}. Reduction for 20 hours in 5%H_{2}/Ar at 930°C. [Ref. 119]

Figure 13; SEM micrographs of exsolved Ni particles after reductions of (La_{0.52}Sr_{0.28})(Ni_{0.06}Ti_{0.94})O_{3} for 12 hours in 5%H_{2}/Ar at 920°C a) before and b) after etching in HNO\textsubscript{3} revealing underlying sockets. Inserts show histograms of particle and socket sizes based on scale bar (200nm). c) shows AFM of sockets similar to those in b. [Modified from Ref. 123]

Figure 14; Micro SOFC architecture based on thin film deposition techniques onto etched Foturan® glass substrate showing a) photograph of 3 cell array and b) schematic cross section. [Ref. 126]

Figure 15; Polished cross-section of thin film interlayer (dense) on a more porous electrolyte both around 1µm deposited by PVD. SEM image taken post-test with electrolyte porosity induced during operation. [Ref. 129]
Figure 1(1).tif
Figure 2(1).tif
Figure 5(1).tif
Figure 12(1).tif
Performance of SOFC are dominated by microstructure, which is a combination of materials composition and processing. Composition tends to dominate the research, however here we focus more on recent trends in processing that aim to develop innovative microstructures for improved Performance, durability and cost.

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