

# PROCESS AND MATERIALS IMPROVEMENTS ON Ni/Cu-YSZ COMPOSITES TOWARDS NANOSTRUCTURED SOFC ANODES: A REVIEW

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**Abstract.** In order to increase the performance of anodes for Solid Oxide Fuel Cell (SOFC) applications, many researchers have sought to synthesize nanostructured powders of Ni/Cu-YSZ by processes such as sol-gel, co-precipitation, deposition, combustion synthesis, infiltration, among others. From these processes, the particles of Ni and/or Cu must be distributed homogeneously in the matrix of YSZ at the nanometer scale. The infiltration process has been seen as a feasible technique to fulfill those requirements. Thus, this work will present the state-of-art regarding materials and processing necessary to obtain Ni/Cu-YSZ nanostructured anodes from nanosized powders aiming to improve of efficiency of these devices by increasing of triple phase boundary size. The manufacturing will be discussed in this review including sintering of nanocrystalline composites.

## 1. INTRODUCTION

Cermets of nickel-based yttria-stabilized zirconia (Ni-YSZ) are the state-of-art anodes of Solid Oxide Fuel Cells (SOFCs), despite some restrictions associated with them. The main reason for their use is the excellent catalytic performance of Ni [1].

The impregnation of Ni-YSZ anodes with certain metals may prevent the occurrence of carbon deposition during cell operation. In particular, Ni/YSZ anodes have been impregnated with copper for the direct use of hydrocarbons as SOFC fuels.

New nanoscale synthesis techniques have emerged with the development of nanotechnology, in order to break down barriers in obtaining these materials. Thus, the use of nanoparticles for obtaining the Ni/Cu-YSZ cermet might generate superior properties and microstructures that were not achieved yet by conventional powder technology

techniques, such as pressing or slip and tape casting [2].

The sintering of nanoparticles might represent a drawback due to an extremely rapid grain growth, leading to the loss of nanocrystalline characteristics and consequently of the anode properties. The goal is to achieve maximum densification while retaining grain sizes at the nanoscale. In this review, the state-of-art of SOFC Ni/Cu-YSZ nanostructured anodes will be presented regarding novel materials synthesis and sintering techniques.

## 2. CERMETS OF NICKEL-ZIRCONIA FOR SOFC ANODES

Cermets of Ni-ZrO<sub>2</sub> were introduced in response to failure of all metal anodes fabricated until now. Ni is the best option as transition metal, but has two major drawbacks. Firstly, Ni has a thermal expansion in-

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compatible with zirconia, which can result in large stresses in the anode-electrolyte boundary, causing fracture or delamination during fabrication and operation as well as loss of physical and electrical contact with the electrolyte layer. Secondly, at high temperatures aggregates are formed by the metal grain growth, thereby blocking the porosity of the anode and eliminating Triple Phase Boundary (TPB) required for the cell operation. Thus, there is a detrimental effect on the performance of the cell [3,4].

To overcome this problem, nickel was associated with the ceramic electrolyte, Ytria Stabilized Zirconia (YSZ). YSZ acts as an inhibitor of Ni grain coarsening during consolidation and operation, and therefore retains the dispersion of the metal particles and the porosity of the anode during long-term operation. Moreover, the introduction of YSZ promotes a coefficient of thermal expansion acceptably close to the other cell components. YSZ also provides a significant contribution to the overall ionic conductivity, extending the length of three phase boundary. Those cermets are chemically stable to high temperatures in a reducing atmosphere [3]. They also allow the anode material to be more resistant in thermal cycles between room and operating temperature [4].

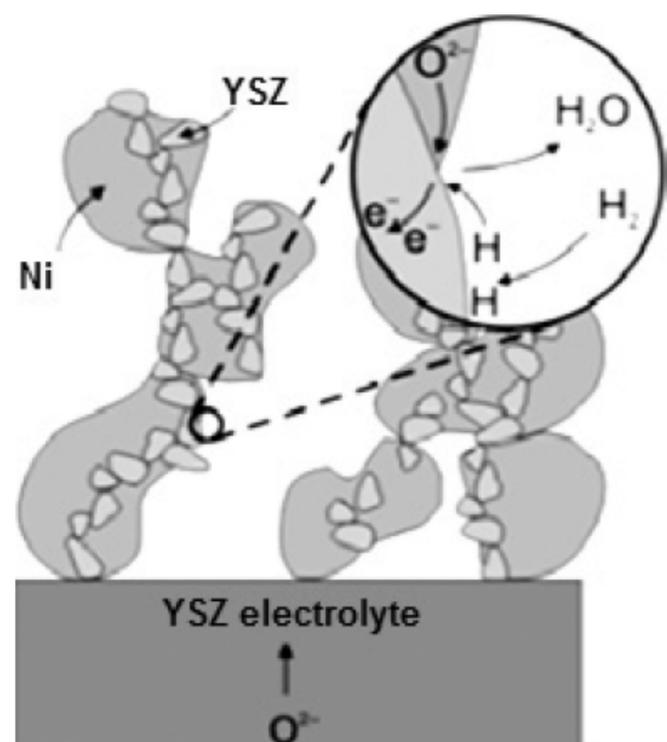
Technical problems related to carbon deposition at the anode still prevent the full use of fuels derived from hydrocarbons [5]. Most of the researches focused on overcoming the limitations of Ni-based anodes have developed alternative anode materials that are catalytically active for the methane and hydrocarbons oxidation and inactive for reactions that lead to C deposition. In addition to these, the tolerance of the material to sulfur is also a desired property. Modification of cermet Ni/YSZ by doping or adding an extra phase has been one of attempts. Copper has been proposed to be added due to its poor catalytic activity for C-H and C-C bond, which inhibits carbon formation [3].

Other compounds such as doped perovskites, particularly (La, Sr)  $\text{TiO}_3$  and (La, Sr)  $\text{CrO}_3$  with added  $\text{CeO}_2$ , are of interest in the construction of "fully ceramic cells" [6]. Table 1 shows some materials proposed for use in SOFCs anodes. Some properties shown can be highlighted, for example, low catalytic activity by incorporating an additional catalyst; chemical compatibility by the preparation of electrodes using the infiltration technique, that will be treated in this paper. All these properties are a function of temperature, pressure and chemical oxygen potential [7].

### 3. TRIPLE PHASE BOUNDARY

The electrochemical reaction takes place in the so called Triple Phase Boundary (TPB) region. This is where the components perform the electrochemical oxidation in the case of the anode. Oxygen anions produced at the cathode migrate through the electrolyte nonporous layer via ionic conduction mechanism. The gaseous fuel diffuses through anode pores reaching the solid surface. Electrons produced by the electrochemical oxidation are conducted to the current collector by reduction of metallic component. It is in the three phase contact (reduced metal, YSZ and gaseous fuel) that the electrochemical reduction occurs at the point shown in Fig. 1 [4].

The higher the TPB, the lowest polarization resistance is expected for the Ni electrode. The area of the TPB is inversely proportional to the radius of the Ni particles. Thus, small particle sizes are desirable to achieve higher TPBs. Ni is suitable for cleavage of both H-H and C-H bondings. Nevertheless, the polarization resistance,  $R_p$ , is unacceptably high for a pure Ni electrode. At temperatures of 800 to 1000 °C, the Ni particles have a high surface mobility, causing sintering and grain growth, reducing the number of active sites. YSZ is added to prevent grain growth of Ni and reduce the aggregate, substantially increasing the TPB area (per unit cell) and controlling the structure and porosity of the

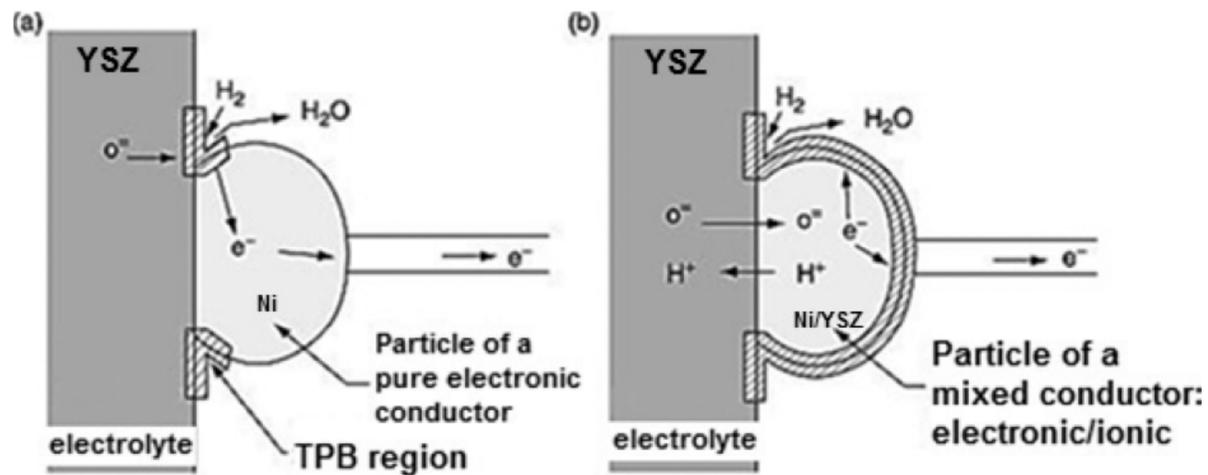


**Fig. 1.** Diagram showing a non-porous electrolyte in electrical contact with a porous cermet anode of Ni/YSZ, as well as an expansion of the TPB region, adapted from [4].

**Table 1.** Comparison of some proposed anode materials for SOFC, reprinted with permission from S. P. Jiang and Y. Yushan, Materials for High-Temperature Fuel Cells (John Wiley & Sons, 2013). (c) 2013 John Wiley & Sons.

Structure	Typical materials	Stability in reducing atmosphere	Ionic conductivity	Electronic conductivity	Chemical compatibility with YSZ	Thermal compatibility with YSZ	Performance using H <sub>2</sub> fuel	Performance using CH <sub>4</sub> fuel	Redox Stability
Mixture	Ni-YSZ	✓	✓	✓	✓	✓	✓	x	x
Mixture	Cu-YSZ	?	✓	✓	✓	✓	✓	✓	✓
Fluorite	YZT, ScYZT, and CGO	✓	✓	x	✓	✓	✓	✓	✓
Cr-perovskite	La <sub>1-x</sub> Sr <sub>x</sub> Cr <sub>1-y</sub> Ti <sub>y</sub> O <sub>3</sub>	✓	?	✓	✓	✓	✓	✓	✓
Ti-perovskite	La <sub>1-x</sub> Sr <sub>x</sub> Ti <sub>1-y</sub> Ti <sub>y</sub> O <sub>3</sub>	✓	x	✓	✓	✓	x	x	✓
Double perovskite	Sr <sub>2</sub> MgMoO <sub>6</sub>	✓	?	✓	x	✓	✓	x	✓
Pyrochlore	Gd <sub>2</sub> TiMoO <sub>7</sub>	x	✓	✓	✓	?	✓	?	x
Tungsten bronze	Sr <sub>0.6</sub> Ti <sub>0.2</sub> NbO <sub>3</sub>	✓	x	✓	✓	?	x	?	✓
Monoclinic space group C2/m	Nb <sub>2</sub> TiO <sub>7</sub>	✓	x	✓	✓	x	?	?	x

(x) Not present; (a) present; (?) unknown



**Fig. 2.** TPB region of different anode materials of a SOFC. a) Electronic (Ni) and b) Electronic/Ionic (Ni/YSZ), adapted from J. Larminie and A. Dicks, [9].

composite. Thus, the larger the size of the TPB, the lower is the polarization resistance [1,4].

Cermets of nanocrystalline Ni-YSZ can offer the advantage of greater TPB to improve the anode performance. The improvement in electrical performance of the anode can potentially reduce the operating temperature of SOFCs when used in conjunction with a suitable electrolyte and thus increasing the reliability and service life of the components by reducing its degradation temperature [8].

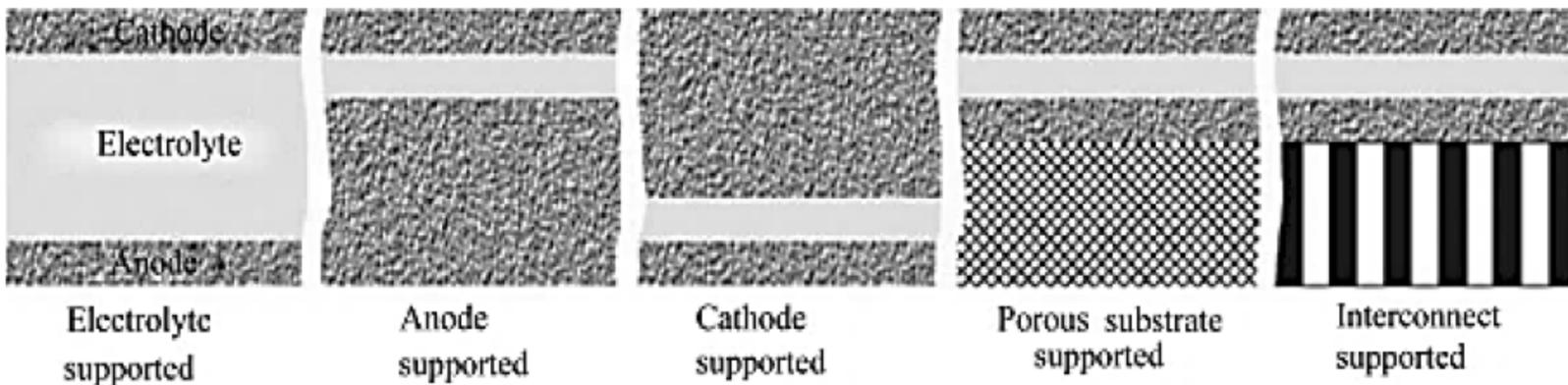
The settings for the TPB of both materials are shown in Fig. 2: (a) pure electronic conductors, e.g. Ni; and mixed electronic and ionic (b), e.g. Ni-YSZ. A higher coverage of the TPB can be observed beyond the anode-electrolyte interface, when mixed conductors are present. This has been described as an offset from the electrochemically active region. Anions of oxygen can diffuse from the further non-porous layer into the electrolyte from the anode porous layer, which increases the TPB [4,9].

The high metal composition in the cermet ensures that the electronic conduction occurs easily, and electrons generated near the anode-electrolyte interface during the oxidation of the fuel reach the current collector. The incorporation of YSZ in the anode to create a cermet material is also important at reducing conditions [4]. In this case, the metallic phase of the cermet anode experiences a considerable degree of shrinkage. There is loss of oxygen anions of the reduced metal oxide lattice which can have adverse effects by the contact between the anode and the electrolyte layer as well as the anode and the current collector. The presence of the YSZ in the cermet, a phase which is not reduced by exposure to reducing environments, allows contact between anode and electrolyte to be maintained at higher levels.

#### 4. REQUIREMENTS FOR ANODES

The anode needs to be chemically resistant to corrosive elements such as O and S. In cases of high polarization, the oxygen concentration in the anode side may increase; then a resistant material to this process is required. Sulfur can block the active sites even at low concentrations. Moreover, at high concentrations, S can have different chemical effects on the cermet metallic phase. The metal must also present a high electric conduction. This will reduce resistive losses and overvoltage. Nickel meets this criterion, but has the tendency to coke formation during hydrocarbon pyrolysis. The activation polarization can be minimized by simultaneously minimizing the particle size of the cermet anode, thereby increasing the TPB. The gas channels through the pores as well as surface diffusion ion transport can be affected by a poor microstructure. The need to improve the anode microstructure also involves maximizing the rates of electrochemical reaction. The area of the TPB has been directly related to the reaction rates of the hydrogen oxidation [4].

The interconnected network of Ni acts as a good catalyst for the electrochemical oxidation of H<sub>2</sub> and provides excellent conduction path for electrons released from this reaction. Furthermore, it acts as a growth and coalescence limiting of Ni particle, and thus, the fine mesh may be maintained after a long time operation at elevated temperatures. The anode performance, in terms of minimal polarization losses and minimal degradation of the electrode, depends strongly on the microstructure and therefore the precursor powders. The network of ionic conduction formed by YSZ particles and the network formed by electronic conduction Ni particles must be long lasting, as well as the TPB between the two networks and the gas phase. Moreover, the relative size of the particles is important because



**Fig. 3.** Different types of cell support architectures for SOFCs, reprinted with permission from Daniel J. L. Brett, Intermediate temperature solid oxide fuel cells (Chemical Society Reviews, 2008. (c) 2008 Royal Society of Chemistry.

YSZ particles need to be much smaller than the particles of Ni to minimize degradation due to sintering of metallic particles and grain growth during operation [10].

The thermal expansion coefficient of the anode is substantially greater than that of the electrolyte and the cathode. In designs of anode supported cells, this can lead to problems of dimensional and mechanical stability. The anode can also be easily oxidized at high temperatures, changing the volume and compromising structure and resistance [11].

The catalytic activity (measure of conversion rate of reactants to products), selectivity (measure of the production of desirable product against undesirable products) and stability in the gas mixture are still the main obstacles for materials used in the electrodes of those cells. Additional parameters affect the performance of the cell including operating conditions such as flow rate, temperature, oxygen to fuel ratio, fuel type, design of gas chamber, among others [12].

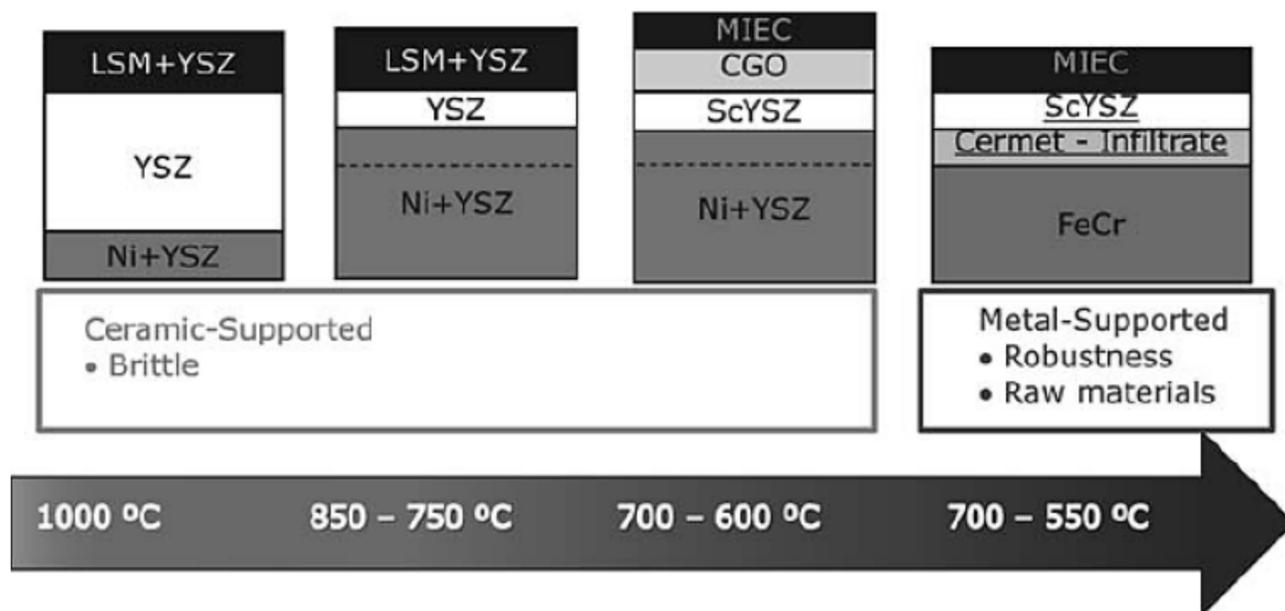
The SOFC anodes must perform four basic functions: (i) transport oxygen anions of 2D external interface (electrolyte-electrode) into the 3D structure of the higher surface area electrode, (ii) transport the fuel from the gas phase to the site of reaction, (iii) catalyze the electrochemical oxidation of the fuel, and (iv) transport the product of electrons from the reaction site for the collector current at the electrode surface. The polarization resistance should be less than  $0.15 \Omega\text{cm}$ . There must be enough open interconnected porosity for the transport of gas ions (YSZ phase) and electrons (Ni phase) within the cell. The region of TPB should have high density and surface area. Ideally, nanometric powders would facilitate the reaction. Mechanical strength should be high enough to support the fine structures used for the cell. Finally, the microstructure must be homogeneous with Ni and YSZ well distributed in the anode [7].

The electronic conductivity of the composites may be significantly lower than that of pure material due to the influence of the barrier pores and electrolyte. For this application, the composite shall present electronic conductivity  $> 100 \text{ S}\cdot\text{cm}^{-1}$ . The electronic conductivity of the composite is a function of the material and percolation constriction, depending significantly on the morphology, the relative sizes of particle, pore size and relative amounts of the components [7].

Depending on the particle size, the percolation of the three phases (Ni, ceramics and pores) is achieved in 30-35 vol.% Ni, that leads to a suitable thermal expansion coefficient. At  $\sim 40$  vol.% Ni, cermetes are electronic conductors ( $500\text{-}1800 \text{ S}\cdot\text{cm}^{-1}$ ) and have a thermal expansion coefficient close to that of YSZ. The smaller the particle size of Ni and electrolyte, the more points the TPB reaction can be expected. The electrochemical activity of the electrodes of Ni-YSZ (expressed as the polarization resistance,  $R_p$ ) reaches values of  $0.15 \Omega\text{cm}^{-2}$  at  $850 \text{ }^\circ\text{C}$  and  $< 0.1 \Omega\text{cm}^{-2}$  at  $950$  to  $1000 \text{ }^\circ\text{C}$ . One of these limitations is the reoxidation of Ni, which involves changes in phase and dimension. The use of thin electrolytes requires a support component that can be an electrode or a supported in electrode. The thickness of the anode substrate may vary from  $100 \mu\text{m}$  to  $2 \text{ mm}$  depending upon the design and strength of the components [13].

## 5. SUBSTRATE-SUPPORTED SOFC CONCEPT

The cell support structures can be classified according to which layer mechanically supports the system: electrolyte, anode or cathode, the porous substrate and metal support structures as shown in Fig. 3. Due to the thickness of electrolyte (typically in the range of  $100 \mu\text{m}$ ) required to mechanically support the other cell components, the elec-



**Fig. 4.** Development trends for planar SOFCs, reprinted with permission from R. Riedel. *Ceramics Science and Technology*, Volume 4, Applications (John Wiley & Sons, 2013). (c) 2013 John Wiley & Sons.

trolyte supported SOFCs are mainly developed for operation at high temperatures ( $> 900\text{ }^{\circ}\text{C}$ ). The substrate may still be anode or cathode or functional porous support providing gaseous diffusion and transport for fuel cell reaction. As the substrate is the main structural component in these cells, it is necessary to improve the conflicting requirements of mechanical resistance and high gas permeability [14].

So far, the most widely concept used is the cell structure supported on anode, due to its high power density and low cost manufacturing. Generally, it consists of a relatively thick support substrate (200 to  $500\text{ }\mu\text{m}$ ) and a thin structure of the anode functional layer. In order to reduce the ohmic resistance of the electrolyte and increase the cell efficiency, the electrolyte deposited layer should be as thin as possible. In general, the film thickness is inversely proportional to pore size and surface roughness, which means that the larger the pore size, the more difficult to obtain a thin electrolyte. Thus, the structure of the anode functional layer requires a structure with a low surface roughness. However, the composite porous support is mechanically weak and may have difficulty withstanding mechanical and thermal stresses generated by the rapid temperature fluctuation [14].

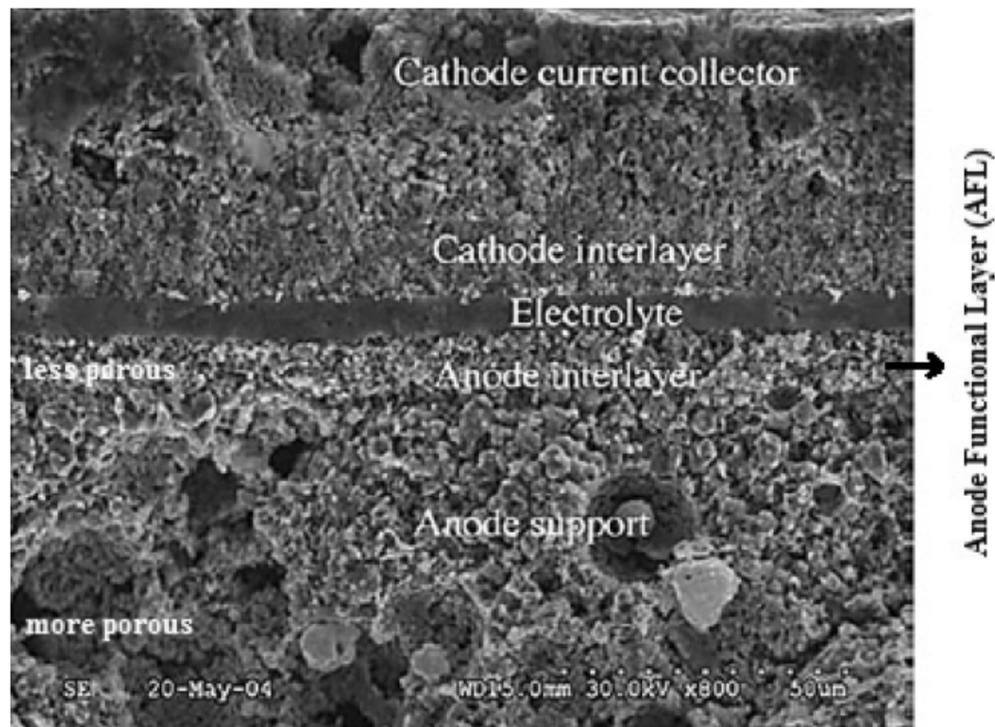
Besides focusing on the development of highly efficient cells, there is the need to reduce costs of the cell. One way to achieve this would be to reduce the operating temperature, which would allow the use of cheaper materials. The central component is the electrolyte, in which the oxygen ion conductivity decreases with decreasing temperature. At operating temperatures above  $900\text{ }^{\circ}\text{C}$ , the elec-

trolyte may be of sufficient thickness to be the support component of the thin electrode layers. To reduce operating temperature of the cell, in the absence of more conductive material, the thickness of the electrolyte must be reduced, so that another component becomes the support layer. Currently, two types of anode-supported cells are in development. For operating temperatures between 600 and  $850\text{ }^{\circ}\text{C}$ , a composite Ni-ceramic material provides support, while for temperatures  $< 600\text{ }^{\circ}\text{C}$  metals such as ferritic steels can be used. The integration of these and other materials with the development trends of planar SOFCs are shown in Fig. 4 [13].

## 6. CONVENTIONAL MANUFACTURING TECHNIQUES

The manufacturing technologies are divided into techniques for the substrate and the cell. The substrate (irrespective of anode, electrolyte, cathode or metal support) is produced mostly by powder technology such as slip and tape casting and pressing. The layers are applied either by thermal techniques such as plasma spraying, or more classical technologies such as screen printing, slip or powder spraying. Additionally, mainly for special layers, thin film techniques can be used. Recently, sol-gel techniques have been successfully applied. The technology that is used for each type of substrate and the functional layer will depend primarily on thickness, roughness and so on. Each technology has advantages and limitations [2].

Tape casting is the most large-scale manufacturing technique used for preparation of substrate anodes made of Ni-YSZ cermets. The casting layer



**Fig. 5.** Cross-sectional SEM micrograph of a SOFC showing the dense electrolyte and porous graded electrodes, adapted from [16].

on the tape is cut and rolled to the desired thickness. Additionally, screen printing and alternative techniques such as suspension deposition (slurry spraying) and dip coating are used particularly when alternative materials electrolytes are being investigated. Faster techniques such as the “dual tape casting” have been developed to prevent delamination and undesirable interactions between the folder of screen printing and the raw materials of tapes [13,15]. After the manufacturing process, the dense YSZ electrolyte layer is connected to a layer of porous Ni-YSZ anode, as shown in Fig. 5.

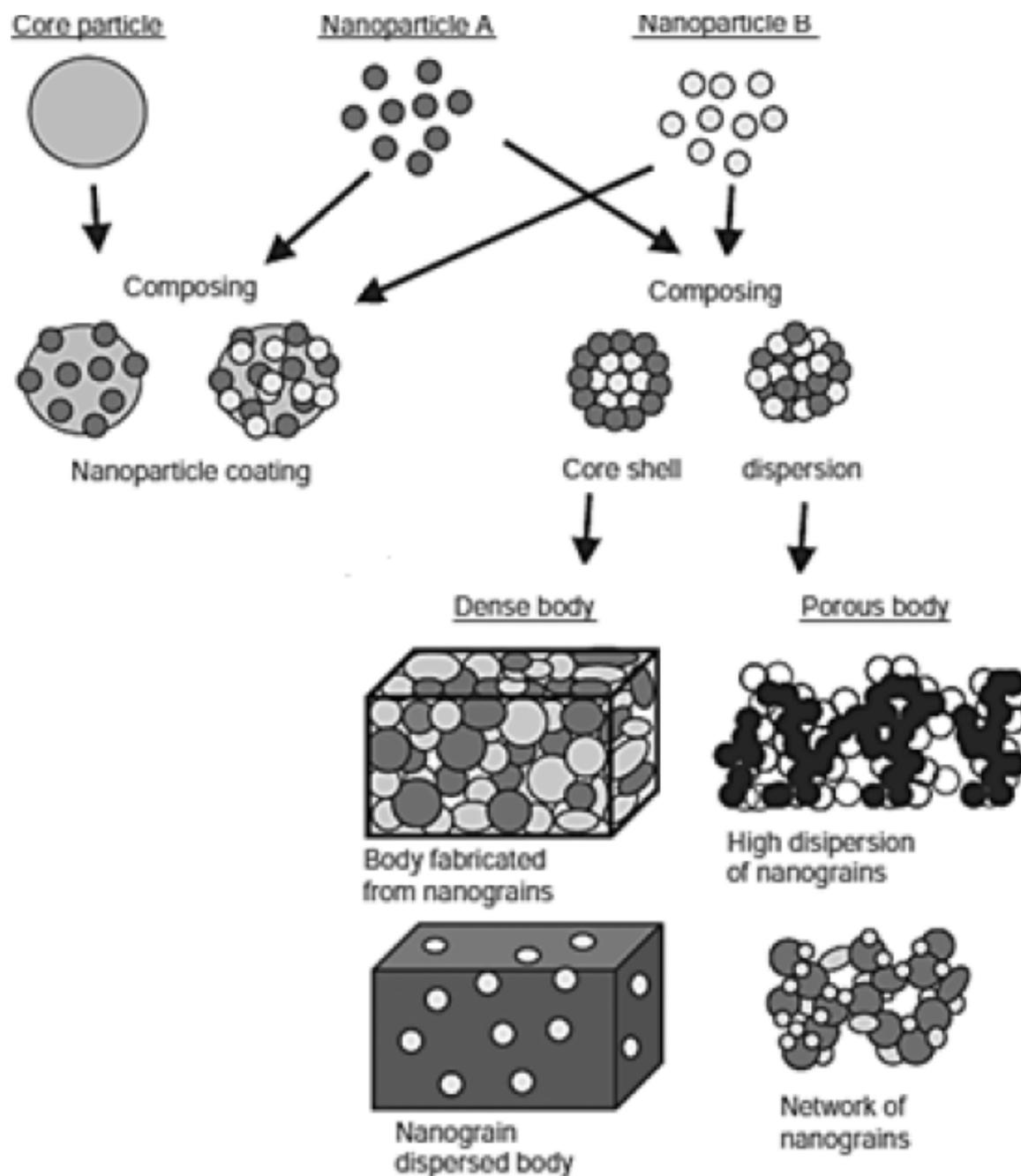
It is important for the YSZ in the electrolyte to be well-connected to the YSZ in the anode because it provides a conduction path for the  $O_2$  ions in the anode, increasing the three phase boundary and availability for reaction. While there is sufficient porosity, so that the gas transfer is not limited, the performance of the electrode increases as the microstructure becomes more refined. This is consistent with the idea that the TPB has to be maximized. Although a fine microstructure with high surface area is clearly desired, this may lead to reduced mechanical strength. The anode is usually used as a mechanical support to the cell, so this can be problematic. As the active region at the anode, where the electrochemical reactions occur, extends less than about  $10 \mu\text{m}$  of the anode-electrolyte interface, a gradual porosity is sometimes used to maximize the amount of TPB in the active region. Thus, high mechanical strength is maintained to the rest of the anode that is used, primarily, in the cell support [16].

## 7. NANOSTRUCTURED ANODES

Engineering at the nanoscale and the focus on the development of nanostructured electrodes for high efficiency and high performance for SOFCs is a relatively recent phenomenon, but the interest in this area has grown rapidly over the past 5 to 10 years [17].

An example of the use of nanostructured materials is the impregnation of nanoparticles, which allow more freedom in the design and selection of materials for SOFCs, and thus, a refinement of the project according to the desired application. Furthermore, the impregnation of the electrode layers results in finely distributed catalyst particles on the surface of the pores, which in turn leads to increased cell performance. The size range of the nanoparticles makes even more efficient the electrode performance. Less catalytic material is needed, since all material is applied on the surface of the layer structure, which may contribute to the response of the electrode. The smaller the particle size, the greater is the number of catalytic sites available for the reaction to occur in the cell [18].

Nanostructured materials are increasingly being employed in SOFCs. Although the primary nanoparticles are generally not stable in materials for SOFCs, due to the heat treatment required to manufacture the cell components ( $> 1000^\circ\text{C}$ ), they usually form nanostructured microstructure with electrocatalytic ion conducting properties and which are different from those of typical polycrystalline materials. Nanoparticles of YSZ (8 mol.% $Y_2O_3$ - $ZrO_2$ ) allow a significant reduction in firing temperature



**Fig. 6.** Nanostructures fabricated from several types of nanoparticles, adapted from [21].

during the membrane formation step of the manufacturing process due to its easiness of sintering compared to polycrystalline powders. For the manufacture of the ceramic substrate, coatings, films and composites, the use of fine ceramic powders as a precursor is of fundamental interest. The ionic charge carriers in electroceramic materials are essentially due to the presence of point defects. So, an increase in the mobility defects density in the region of loading, as a result of a significantly large area of interface and grain boundaries in nanostructured systems, lead to an electrochemical behavior completely different from those of polycrystalline materials [18].

Nanomaterials can present two main effects on SOFCs: reduce the processing temperature and increase performance ( $W/cm^2$ , use of fuel). These effects promote the reduction of manufacturing costs, increased reliability, reduced operating costs and system as a whole and promote a faster initial starting cell. Moreover, these nanoscale materials provide improved performance of the electrodes by

reducing the particle size that causes an increase in surface area of the material and interfacial turn. Thus, there is an increase in TPB and thereby a higher efficiency of the cell. The current barriers of these materials include: stability in operating temperatures (650-800 °C), difficulty of incorporating the processes of tape casting, aggregates, and high cost of processing [19].

Nanoparticles are defined as “fundamental fine particles with sizes in the nanometer region formed with their retained chemical characteristics, which differ significantly from those in the bulk form” [20]. The increase in surface area by reducing the level of fine particles increases their original chemical and physical characteristics as materials or particle extensively. For example, it increases the reactivity of each particle enabling low temperature sintering of ceramic and providing improvements in their role as catalytic activity. However, it tends to produce physically and chemically unstable states due to the large increase in surface energy. Nanoparticles are difficult to exist independently and are subjected

**Table 2.** Relationship between the functionality of SOFC electrodes and nanostructures, reprinted with permission from H. Tsujimoto and Y. Kawashima, Nanoparticle Technology Handbook (Elsevier, 2012). (c) 2012 Elsevier.

Function	Nanostructure necessary for the function
Electrode reaction characteristics	Constituent particles of the electrode should be nanoscale, uniform and highly dispersed
Electron and ion conductivity	Networks of constituent particles of the electrode
Diffusion and ion conductivity	Proper pore size, pore size distribution and porosity
Strength, heat and chemical stability	Binding force of electrode constituent particles and proper microstructure

to particle agglomeration, grain growth by sintering and other changes of state by oxidation and other reactions. Such low stability, dispersibility and workability have prevented the wide application of nanoparticles [21].

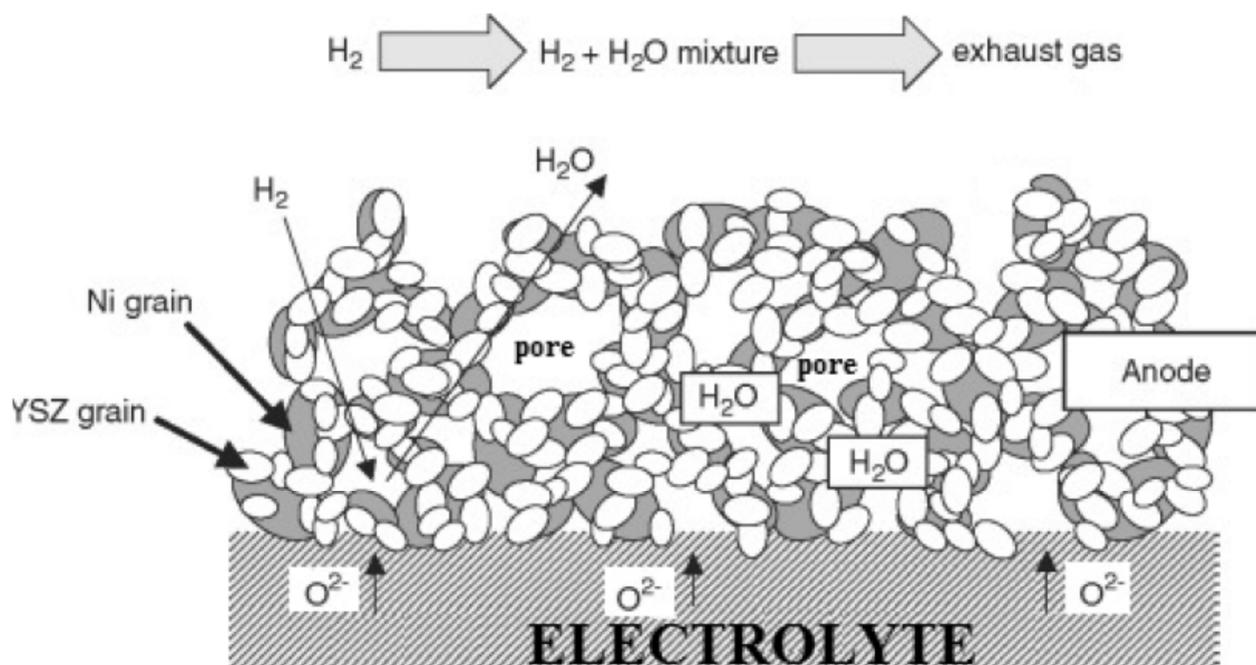
As a means of dealing with these problems, the application of nanoscale structures is being developed carefully. The inherent characteristics in nanoparticles can be maintained while reducing its reactivity for nanostructure manufacturing. Thus, fully stable materials using the functions of nanoparticles can be built by manufacturing of composites and bulk materials from nanoparticles depending on their intended use. Nanostructures play an important role in the current nanoparticles application. Typical images of nanostructures as well as composite nanoparticles, porous and dense, are illustrated in Fig. 6, where two types of nanostructures composed of nanoparticles and main micrometric particles are exemplified. Nanostructures can be found as connected nanograins in dense bodies or as dispersed nanoparticles in a dense matrix or porous network. Composite structures may have nanoparticles as

catalysts fixed on the surface of carrier particles in order to generate high catalytic activity [21].

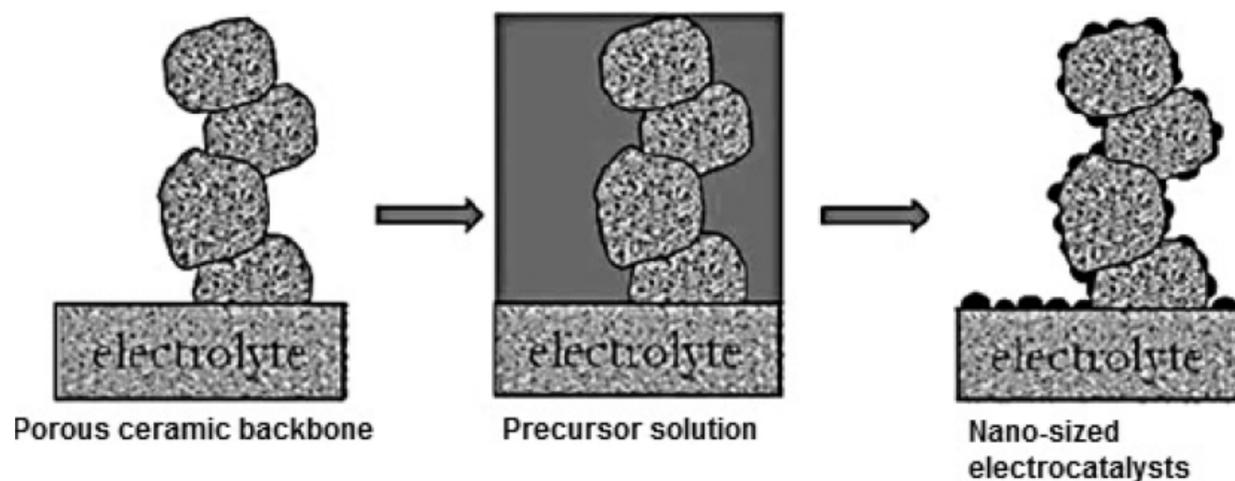
The relationship between the functions of SOFC electrodes and porous nanostructures is shown in Table 2 and an example of the Ni-YSZ anode structure in Fig. 7. Necessary functions are dependent on structure, and functions of the electrode are improved by controlling the same. In the case of Ni-YSZ anode, the following is required by the structure [21]:

- Increasing of reactive interface for both Ni and YSZ, due to their microscopic, homogeneous structure and high dispersion, provided that the reaction occurs at the electrode in the Ni and YSZ interface.
- Networks of Ni and YSZ in the manufacture of fine paths for electrons and ions.
- Proper porous structure for fuel diffusion and reaction gas.
- Association of constituent particles and thermo-set structures in order to achieve higher thermostability and resistance.

The electrode structure obtained from composite nanoparticles is constituted from a porous net-



**Fig. 7.** Morphology control of Ni/YSZ cermet anodes, adapted from [21].



**Fig. 8.** Active materials impregnation on porous ceramic backbone, reprinted with permission from R. Riedel, *Ceramics Science and Technology, Volume 4, Applications (2013, John Wiley & Sons)*. (c) 2013 John Wiley & Sons.

work structure, where Ni is partially surrounded by microscopic YSZ. Surrounding Ni with microscopic particles of YSZ not only allows the reactive interface to expand but facilitates grain growth control of Ni particles during operations at high temperatures (1000 °C). As a result of long-term evaluation of power generation, the performance of the electrode reaction was demonstrably improved and stability maintained [21].

## 8. SINTERING

For developing high-performance SOFCs, it is necessary to create a large area of high reactivity with reaction at the electrode to achieve a low internal resistance and good morphological stability of the cells at elevated temperatures, while ensuring the passage of liquid and gaseous reactants. Therefore, porous electrodes made of well-dispersed fine particles are highly desirable. However, sintering of electrodes (anodes) usually causes increased grain size of Ni particles. This leads to the formation of large particles in the Ni anode resulting in inhomogeneity in the structure. The binding of YSZ nanoparticles on the surface of Ni needs to suppress grain growth of Ni to increase SOFC power density and stability in large scale [22].

The thermodynamic driving force for sintering of nanoparticles is extremely large. In this context, the sintering involves connecting a solid particle to another. Sintering consists of two closely related processes: densification and grain growth. A unique feature of the nanoparticles is that usually they experience an extremely rapid grain growth, making the loss of nanocrystalline characteristics of the sintered state. Regarding the manufacture of bulk nanocrystalline materials from the nanoscale, the goal is to achieve maximum densification while re-

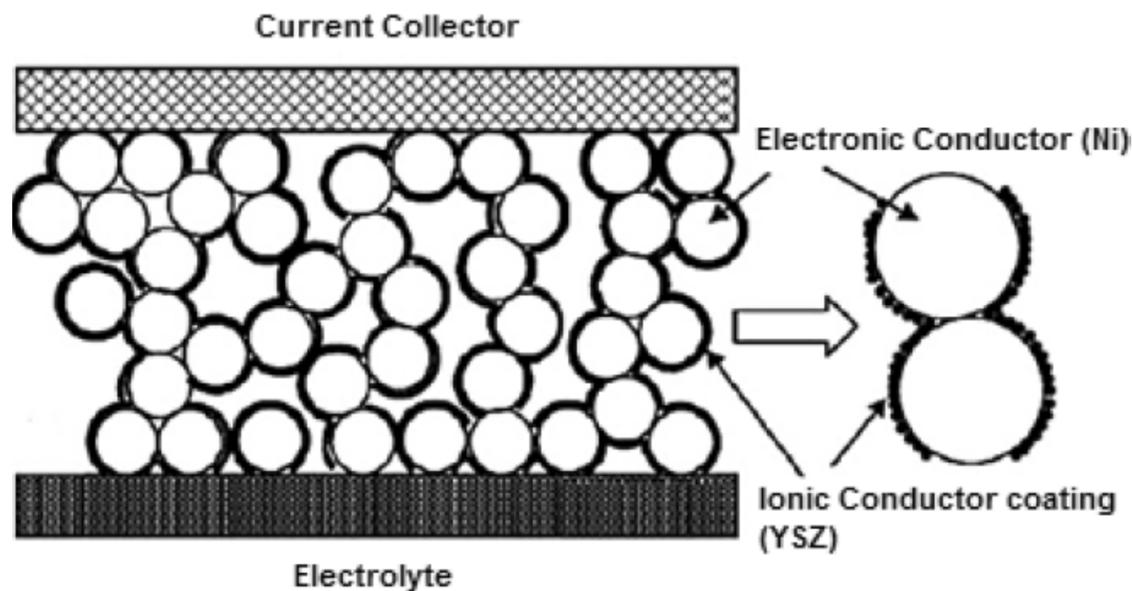
taining grain sizes at the nanoscale. This goal, however, has been very difficult to achieve [23]. It is already known, for example, studies of nano YSZ sintering have shown that the sintering temperature of the nanocrystalline  $ZrO_2$  starts at temperatures of 200 °C lower than microcrystalline powders [24].

## 9. NOVEL MANUFACTURING TECHNIQUES

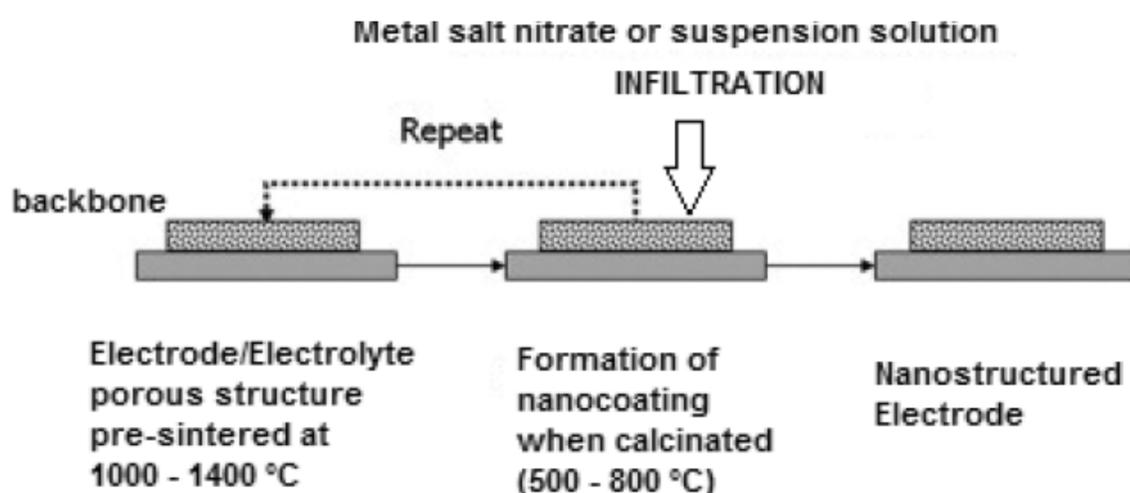
Ni-YSZ anodes are generally prepared by mechanical mixing or milling of individual powders followed by pressing and sintering. Although these methods are simple and provide precise control of chemical composition, it is difficult to achieve a homogeneous distribution of constituents, which results in unsatisfactory performance. A homogeneous distribution of fine powders is a prerequisite for better performance of an anode [8]. In this way, new techniques like infiltration emerge to fulfill these requirements.

The infiltration method may develop better electrodes as it expands the selection and combination of electrode materials by minimizing the mismatch in the coefficient of thermal expansion and the removal of potentially harmful reactions between the electrode material and electrolyte [17]. Using nanoparticles with high ionic conductivity and/or excellent catalytic activity is an effective approach to improve the performance, stability and tolerance of the Ni-based anodes via wet impregnation techniques [25].

In SOFCs, the electrochemical reaction takes place mainly in the working electrode layers (a few tens of  $\mu\text{m}$  thick), which are in contact with the membrane of the ceramic electrolyte. The functional layer contains fine particles of the electronic and ionic conductor material. These functional layers can be distinguished from the thicker support contain-



**Fig. 9.** Schematic diagrams of a sphere-packed electrode coated by impregnated nanoparticles, adapted from [25].



**Fig. 10.** Typical process of infiltration metal salt solution or suspension of nanoparticles in a pre-sintered porous structure of the electrode, adapted from [17].

ing ceramic particles of larger sizes. A high surface area of the electrocatalyst on the functional layer is required to increase the rate of reaction and promote direct electrochemical oxidation of hydrocarbons (fuel). The high surface area can be obtained by the infiltration or impregnation methods, for example [18].

Direct synthesis of the electrocatalyst layers, a principle shown in Fig. 8, consists in impregnating generally a nitrate solution into a porous electrode (backbone or skeleton) that is decomposed by heating and then reduced to form the surface layers in the nanometer order. Infiltrating precursor solutions are typically of Ni and Cu and  $\text{CeO}_2$ , which by decomposing and reducing form nanoparticles on the surface of the skeleton [13].

A theoretical model has been proposed by Zhu et al. [26] combining the electrode with the spherically packed support whose surface is coated with nanoparticles of the second phase as shown in Fig. 9. Ding et al. also demonstrated that the size increases with the load TPB coated nanoparticles and it is dependent only a load before the maximum for

monolayer coating [27]. Additionally, the maximum load increases with the porosity of the support, thus prolonged TPB can be achieved by increasing the porosity of the structure of the pre-sintered electrode and the loading of the impregnation phase within a maximum amount [25].

The key to developing this technique is overcoming the high temperature processing via deposition of electrochemically active nanoparticle into the rigid skeleton and pre-sintered electrode by infiltration technique. The process involves precipitation and decomposition of a metal salt solution into a porous structure electrode, as discussed earlier, forming a discrete distribution or a continuous fine network on the surface. Fig. 10 shows a schematic view for typical synthesis route of a continuous layer deposition of nanoparticles on a pre-sintered electrode via infiltration of a suspension of metal salt, which may be facilitated in vacuum. Thus, this layer will have a high electronic conductivity and electrocatalytic activity, although a multi-step infiltration is necessary to achieve that electronic conduction [17].

The results from this technique showed that the infiltration of metal nanoparticles and metal oxides not only increases the TPB, but also has an important role in enhancing the catalytic reaction with fuel within the cell. The catalytic role of this nanoparticle film depends on both the morphology and microstructure of the infiltrated phase and the nature of the support structure [17].

The advantage of this process is that the porous electrode may be infiltrated by a nanosized electrocatalyst, which is subsequently processed at significantly lower temperatures than those required to achieve the final density of the ceramic electrolyte and a good electrolyte-electrode interface [18].

## 10. CERMETS OF COPPER AND NICKEL-ZIRCONIA FOR SOFC ANODES

Cu alloys with more refractive metals such as Ni and Co have been used in infiltrated anodes in an attempt to increase the thermal stability. Fuel cells with anodes infiltrated, in which a Cu/Ni alloy was used for collecting current, have been shown to be more tolerant to hydrocarbons than those produced by conventional anodes composite Ni/YSZ only. Mixtures of Cu and Co have shown more potential, especially when used methane as fuel. Unlike Cu/Ni, Co and Cu do not form alloy and separate into two phases when mixed. Anodes in which both Cu and Co have been added by the infiltration of Co particles appear to be more widely covered by a thin layer of Cu. This is due to the low surface free energy of Cu compared to Co. Cu coating passivates the catalytic activity of Co and these composite anodes have lower activity for the formation of carbon deposits [16].

Cu-based anodes were initially developed for the direct oxidation of  $\text{CH}_4$ . Unlike Ni, Cu is relatively inert to the formation of C-C bonds, but its melting temperature is 1083 °C, significantly lower compared to Ni (1453 °C). Thus, the cermet anodes based on Cu cannot be produced using the same method used for anodes in the Ni-based cermets. The alternative method involves impregnating a solution of  $\text{Cu}(\text{NO}_3)_2$  in a skeleton of YSZ prepared on a dense layer of electrolyte YSZ, followed by calcination to decompose the nitrate and oxide form [28].

The thermal stability of Cu is a barrier since the cell operates relatively close to the melting point of Cu (1085 °C), with the thermal stability of the Cu phase being a function of the infiltration technique.

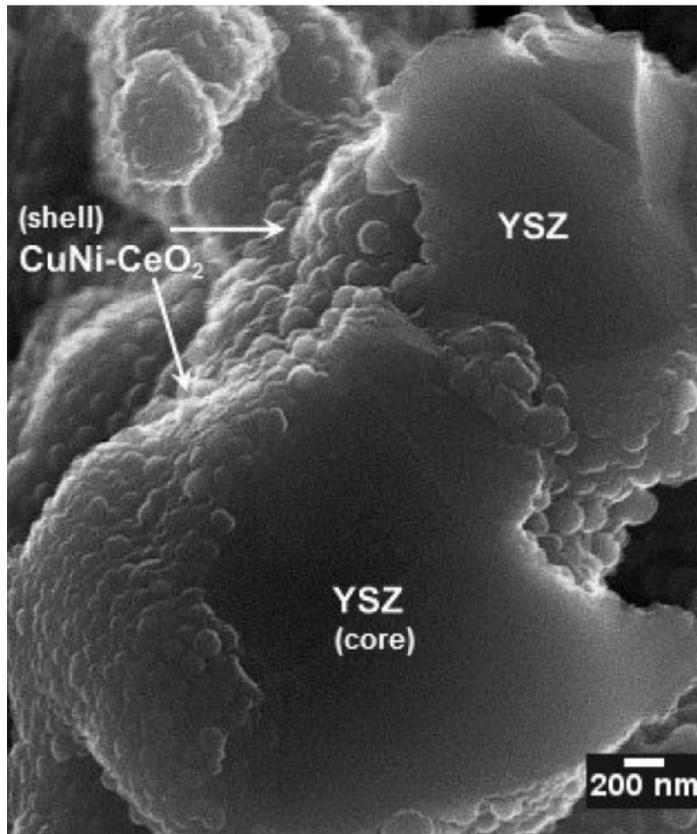
The bimetallic materials can increase the melting point and add stability to the anode. However, the addition of another solid phase hinders the design of the anode TPB. In this case, there would be four phases: electrolyte, electronic conductor, electrocatalyst and gas phase, all of which should be very close to create a functional anode [7].

Cu-YSZ composites produced by infiltrating the Cu precursor into a preform YSZ skeleton can reach conductivity of  $1000 \text{ S}\cdot\text{cm}^{-1}$  with Cu at 15 vol.%. This amount is much lower than typically required for percolation in Ni/YSZ anodes (40 vol.% Ni) manufactured by mixing powder of NiO and YSZ. High conductivity at low loads is due to the selectivity of the coating on the pores of YSZ to create a contiguous surface layer. The total electronic conductivity of the composite required is dependent on the thickness of the anode. Low conductivities can be overcome by the use of thin anode, but this requires that one of the other components, the cathode or the electrolyte, is denser and triggers the mechanical support of the cell [7].

There is no single material that can adapt to the electronic conductivity and electrocatalytic activity of Ni in  $\text{H}_2$  fuel. Thus, multicomponent electrodes are required, with each component gathering only one or perhaps two functional requirements, for example, a matrix of ion-conductive YSZ partially filled with a material thermally stable and chemically compatible with high electronic conductivity. Catalytic activity can then be added by inserting a secondary transition metal on the surface. The main disadvantage is that the TPB has a higher complexity in the reaction mechanisms that involves more than two solid components to achieve the necessary requirements. This is feasible when considering recent advances in microstructural analysis with the advances made in controlling the microstructure via infiltration [7].

The specific process can be described with particular infiltration of salts of  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  dissolved in deionized water, calcination in  $\text{H}_2$  at 950 °C during 30 min to obtain a nanolayer of particles adhered on the surface of the Ni-YSZ structure. While  $\text{H}_2$  is used as a protective atmosphere, where the anode is oxidized, producing CuO internally, this compound is reduced in situ during the cell operation. Finally, the process is repeated a number of times for the complete adhesion of Cu on the pore walls of the substrate [29].

An image obtained by SEM shows the microstructure of a single cell prepared (Fig. 11). By infiltration of the microemulsion precursor  $\text{CuNi-CeO}_2$



**Fig. 11.** SEM cross section of YSZ structure infiltrated with the precursor microemulsion  $\text{CuNi-CeO}_2$ , followed by calcination at  $450\text{ }^\circ\text{C}$ , adapted from [30].

and subsequent calcination above  $450\text{ }^\circ\text{C}$  a thin film of catalyst (50-200 nm) is formed, which covers the whole structure of YSZ [30].

The impregnation with metals (Cu, Ag, Sn) prevents the occurrence of carbon deposition, in particular, the impregnation of Cu into the anodes Ni/YSZ and  $\text{CeO}_2/\text{YSZ}$  has been investigated for the direct use of hydrocarbon fuels. The preparation of anodes for impregnation, however, it takes hours if not days so that a large number of impregnation steps and subsequent calcination are required for insertion of the desired amount of metal. Then, there is a need to develop a method for preparing carbon tolerant anode in less time [15].

## 11. DESIGN AND COMPOSITION OF FUEL CELL COMPONENTS

Based on the design of SOFC planar cell structure type due to its easiness of fabrication and potential for the generation of high power densities compared to other configurations of cells, for a anode supported SOFC, the operating temperature can be decreased to approximately  $800\text{ }^\circ\text{C}$  or less (depending on the electrolyte film thickness) without compromising power output. This allows the device to be manufactured with low-cost materials. The design of cells in flat format offers increased performance and high power densities compared tubular configurations. The conduction of flat cells enables the internal resistance loss is independent of cell

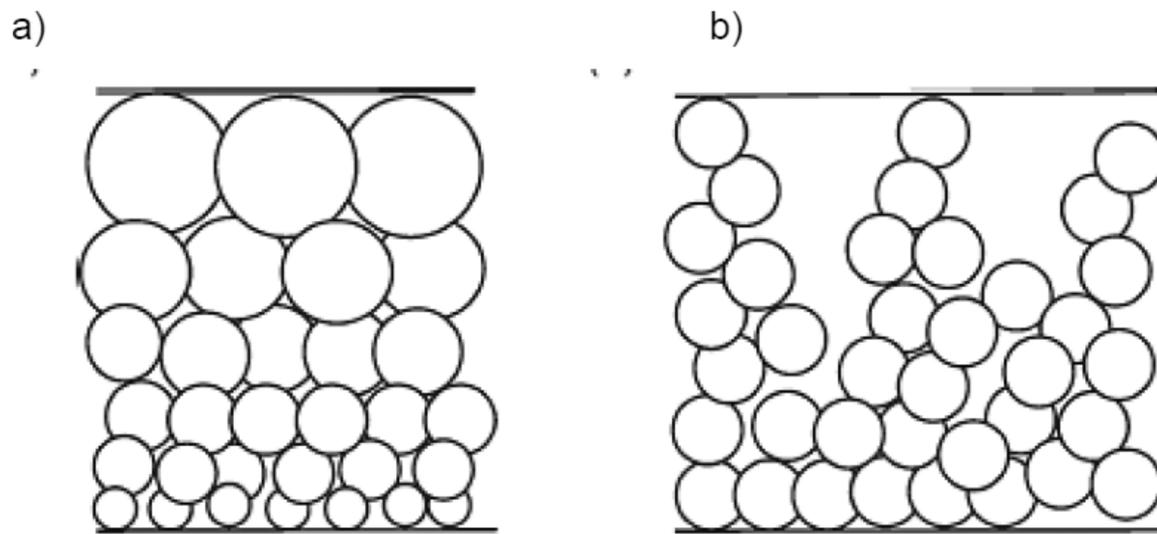
area. Thus, the cell components can be produced with this reduced thickness to minimize resistive losses [31].

Parameters that are used to control the properties of cermet are: (i) the volume fraction Ni/electrolyte (YSZ); (ii) additives such as nanoparticles of other elements such as Cu; (iii) the chemical composition of electrolyte component (YSZ), and (iv) porosity and pore size distribution, which is mainly affected by morphology of the raw material, methods of application and production parameters such as sintering and nanoparticle infiltration of active electrocatalytically nanoparticles. The properties of various electrodes are deeply related with these parameters, but also strongly associated with the atomic-scale structure of the Ni-electrolyte interface, which in turn is affected by segregation of the components and impurities as well as poisoning in the gas phase [1].

The anode cermet material has two paths designed with electronic and ionic conductivity for Ni and YSZ component, respectively. Ni provides the primary means for driving the material through the anode with a considerably higher conductivity than YSZ at typical operating temperatures ( $600\text{-}1000\text{ }^\circ\text{C}$ ). Therefore, a continuous path for electron conduction is required through the cermet anode. The proportion of metallic and oxide components must be carefully designed to produce a cermet material with desired electronic conductivity. For the experiment, the transition from cermet material which is ionically conductive and electronically conductive occurs which is between a Ni content of 30 to 40 vol.%. It is noted, however, that the proportion of the metal component in the cermet is not the only factor to be considered since the microstructure can affect the overall conductivity of the material, thereby justifying the optimum content range given [4].

The electrical conductivity increases as the surface area of the YSZ component decreases. The smaller the particle sizes of Ni, the higher the conductivity derived from the ability of Ni particles in contact with other conductive particles. Furthermore, it has been shown that a microstructure composed of smaller particles produce a lower charge transfer resistance. This is supported by research showing that the electrode with a smaller proportion will present a lower resistance due to increased TPB [11].

A new way of producing electrodes is the functionally graded electrode, i.e., varying the composition or structure gradually from the interface electrolyte/electrode to the free surface of the electrode. Through mathematical modeling and experimental



**Fig. 12.** A schematic microstructure grading: a) Particle size grading and b) porosity grading, reprinted with permission from L. Liu et. al., Modeling of Solid Oxide Fuel Cells with Particle Size and Porosity Grading in Anode Electrode (John Wiley & Sons, 2012), (c) 2012 John Wiley & Sons.

efforts, functionally graded structures have been revealed in the increase power output of the cell [32].

### 11.1. Particle size grading

A schematic of the characteristic degree of particles size of the SOFC anode microstructure is illustrated in Fig. 12a. A microstructure of the electrode with a larger reaction area of the TPB and high diffusion capacity can significantly increase the performance of a SOFC. It is known that the smaller the particle size of the structures the larger the area of the TPB, but it will have a lower diffusion coefficient due to smaller pores. On the other hand, for larger particle sizes, the area TPB is smaller and the diffusion coefficients are increased. Therefore, a particle size of the anode can take advantage of the larger area of the reaction TPB near the anode-electrolyte interface where the reaction occurs primarily and without suffering from high losses induced by the use of larger particles near the free surface [32].

### 11.2. Porosity grading

The lower the porosity, the larger specific reaction area of the structures will be. However, the diffusion coefficients will be low due to small pore sizes. Fig. 12b shows a schematic of the characteristic degree of porosity of a SOFC anode microstructure. It is known that higher porosity structures lead to larger diffusion coefficients and a larger TPB reaction area as seen in Fig. 11. Larger TPB reaction area results in reduced activation losses, since activation energy is dependent on catalytic material, temperature, area, and reactant gas pressure. Anode graded porosity can take advantage of the high area next reaction to the anode-electrolyte interface and not

be subject to high diffusion losses by using a higher porosity at the free surface. The range of the porosity is limited to values of 10-60%. This range is chosen because the structures with high values are mechanically weak and difficult to produce structures with smaller values as limit gas diffusion. Generally, high-performance anodes are 30-40% porous [32].

## 12. PROSPECTS IN SOFCs MARKETS

The market of SOFC systems is until now hampered by two drawbacks: firstly, manufacturing costs of all components, and secondly, the short life span (or high rates of degradation). Especially for stationary applications, a lifetime of over 40,000 h (4.5 years) of operation is sought and degradation rates, in terms of voltage losses, should be smaller than 0.5% in 1000 h. Also, many works are focused on reducing manufacturing costs and increasing the life of SOFC components. The following targets are sought [2]:

- Enhancing power density, i.e. lowering the amount of necessary components and therefore the cost per system;
- Reducing the size of components to minimize material costs;
- Implementing techniques of mass production for the cell;
- Reducing the operating temperature of the system to minimize the phenomenon of thermally activated degradation and introduction of cheaper materials.

## 13. CONCLUSION

According to this review, it is feasible to obtain nanostructured Ni/Cu-YSZ anodes from

nanopowders for application in SOFC. Infiltrating of Cu in a backbone structure of Ni-YSZ ceramic is a way to overcome some technological drawbacks, such as the low melting temperature of 1083 °C, being possible to add it after the backbone is manufactured. Moreover, copper has poor catalytic activity for C-H and C-C bond, which inhibits carbon formation being appropriate for SOFCs with hydrocarbons as fuels.

It is believed that the manufacturing of nanostructured anode composites by infiltration will bring an improvement of the TPB region. In this way, it may increase the reaction sites and reduce the potential contamination by adding multi-components and improving the cell operating performance. There is still a long path to enhance the performance of these devices and nanotechnology may play an important role in this area.

As reviewed in this work, many special properties can be manifested when it comes to nanometer dimensions. However, there are still many challenges regarding the generation of those composites from the initial synthesis to the final production of the cermet material.

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