Nanotechnology for improving solid oxide fuel cells

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The emergence of nanotechnology in recent decades has given a great deal of new insight into theories previously widely assumed by the scientific community. This has resulted in industry showing considerable interest in nanostructured materials, often thanks to the possibilities of new, highly desirable properties, absent in bulk phases. The use of nanomaterials has typically been restricted to low temperature devices, however advances in solid oxide fuel cells (SOFCs) such as lowering operating temperatures allow new possibilities for their application. The most advantageous property of nanomaterials for SOFC application is their high surface area to volume ratio, which results in the increase of the active electrode area. In this chapter several nanomaterials from zero- to three-dimensional have been discussed, providing an overview on the development of novel nanostructures and a comprehensive understanding of their electrochemical behaviour for intermediate temperature SOFC (IT-SOFC) application. In addition, the present and future prospects of these materials are also discussed, revealing the increasing importance of these nanomaterials when the operation temperature is decreased.

Keywords: SOFC, Nanomaterials

1. Introduction

Fuel cells are electrochemical devices that directly convert chemical energy to electrical energy. Lowering the operating temperature to the intermediate range (500–700 °C) has become one of the major challenges for solid oxide fuel cell (SOFC) researchers. These low temperatures, however, encourage an increase in cathode polarization significantly reducing the overall cell performance. This is caused by the high activation energy associated with the oxygen reduction reaction at the cathode side. This limitation can be overcome in one of two ways; the development of new, improved cathodes or the incremental optimisation of known materials. Recent novel materials include layered structures such as Ruddlesden-Popper [1,2] or double perovskite-structured phases. Often, as in the case of many double perovskites, showing lower activation energy of the oxygen reduction processes, demonstrating their suitability for operation at reduced temperatures [3-6]. Examples of incremental advances are the creation of composite materials, enhancing properties such as ionic conductivity or thermomechanical compatibility. Of these, nanocomposites, which include zero-dimensional nanostructures, emerge as the most promising for enhanced electrochemical behaviour [7,8]. An additional example is the microstructural optimisation in one-, two-, and three-dimensions (1, 2 and 3D). Improvement of electrochemical behaviour can be achieved through extension of the active triple phase boundary (TPB) by increasing surface area [9]. In this chapter a brief review of the different nanostructures for SOFC application is presented, highlighting the improvements possible through use of nanostructured materials.

2. 0D Nanomaterials

Zero-dimensional (0D) nanostructures are those in which none of the dimensions exceed the nanometric scale, an example of which is individual nanoparticles. Although perovskite-structured nanoparticles are frequently reported in literature for cathode application [10-12], in order to be considered 0D in nature they must be dispersed and otherwise can be treated as three dimensional (3D) nanomaterials, discussed later. 0D nanomaterials for SOFC application therefore primarily consist of those infiltrated into electrodes in order to improve their electrochemical properties. These are frequently composed of fluorite-type materials, such as gadolinium/samarium doped ceria (GDC/SDC), or zirconia based materials, such as yttria-stabilized zirconia (YSZ) [13-18]. These materials are typically employed as electrolytes due to their fast ionic conduction and their use in electrodes is thus targeted at improving this aspect. Although several studies highlight the importance of microstructural optimization, using 1D, 2D or 3D nanostructures, very few have focused their attention on the deposition of nanoparticles (0-D nanostructures) into an established electrode skeleton. This last approach, usually done by the wet impregnation technique, has been used extensively in the preparation of heterogeneous catalysts, but only recently has found application in SOFCs [19].
2.1 Infiltrated/Impregnated 0-D nanostructures

2.1.1 Ceria based 0-D nanostructures

Cathode materials are commonly based on perovskite type oxides. These oxides present high electronic conductivity but their low ionic conductivity is often a limitation, presenting a barrier to oxide ion migration from potential sites of oxygen reduction reactions (ORRs) to the electrolyte. The introduction of an ionic conductor should therefore be useful in achieving higher performance. If the interest in reducing the SOFC operation temperature is also considered, an ionic conductor with sufficient performance in the intermediate temperature range would be the best option for infiltration, creating a composite cathode material. CeO$_2$ based 0D nanostructures are the most commonly infiltrated materials, with wet impregnation of CeO$_2$ and Gd-doped CeO$_2$ typically carried out by placing a drop of (Sm$_{0.2}$Ce$_{0.8}$(NO$_3$)$_x$) or (Gd$_{0.1}$Ce$_{0.9}$(NO$_3$)$_x$) solution on top of the coating allowing infiltration into the electrode skeleton by capillary action. Often the addition of ethanol into the aqueous solution is made, with a ratio of approximately 1:1, improving wettability with the electrode backbone [13]. The sample is subsequently air-dried and thermally treated in order to decompose the nitrates and form the desired crystalline phase (> 600ºC) [20,21]. Additional infiltration can be achieved through repeating the process. High amounts of the ceria based 0-D nanostructures do, however, have the potential to limit the ORRs due to its ionic conducting nature, reducing active area and thus performance. The proportion of ionic conductor, in both conventional composites and nanostructured composites, consequently rarely exceeds 30% [22]. The discussed synthesis route leads to a near homogeneous distribution of 0D nanostructures within the perovskite skeleton, although heterogeneity is often present in the least accessible regions adjacent to the electrode/electrolyte interface.

2.1.2 Precious metal 0D nanostructures

Precious metals are employed as catalysts for a range of applications, including energy storage devices [23], low temperature fuel cells [24], hydrogen generation [25,26] and car catalytic converters [27]. Due to their high operating temperatures, the catalytic effect of precious metals is not required for SOFCs. Several authors have, however, reported significant improvements to the ORR by the creation of 0D precious metal nanostructure/perovskite nanocomposites [28-32]. In spite of the improved performance of electrodes with the addition of precious metal nanoparticles, their use in SOFC devices is not desirable to their high, volatile cost. These materials and their effects will therefore not be further discussed.

![Fig. 1 0D precious metal nanoparticles: a) Au nanoparticles, b) Ag nanoparticles.](image)

2.2 Effects of the infiltrated 0D nanostructures

2.2.1 Thermal expansion coefficients

SOFC electrodes require good compatibility between their thermal expansion coefficient (TEC) and those of other cell components. Significant mismatches are often present between cathodes and electrolytes, a particular problem for materials containing cobalt [33]. The addition of ionically conducting nanoparticles has the beneficial side effect of cathode TEC, improving compatibility with the electrolyte [34,35]. As cobaltites present high electrochemical performances as SOFC cathodes [36-39], the infiltration of 0D nanoparticles should allow wider applicability of these materials without affecting the mechanical stability of the cell.

2.2.2 Ionic conductivity

While perovskite oxides can be mixed ionic and electronic conductors the level of electronic conduction is significantly higher than that of ionic. While the presence of ionic conduction makes them excellent materials for the ORR the low
level remains the limiting factor. Infiltration of ionically conducting nanoparticles has been found to enhance the overall performance of the cell [40].

2.2.3 Electrochemical performance

In both conventional and graded electrodes, the infiltration of 0D ionically conducting nanoparticles is expected to influence oxide ion diffusion across the electrode towards the electrolyte, as previously discussed. This process is known to contribute to the medium frequency (100-1000 Hz) response measured by impedance spectroscopy [12] which dominates cell resistance and should be reduced with nanoparticle infiltration [16]. Nevertheless, as previously discussed, high proportions of these particles could limit the active area for the ORRs [41]. Another strategy to enhance ionic conductivity without affecting active area is the creation of gradual composites [42]. In these electrodes, the amount of ionic conductor increases towards the electrolyte, while the outermost regions, where the ORR becomes crucial, contain minimal quantities of these particles. This strategy is considered very promising, however further studies are still required.

3. 1D Nanomaterials

One dimensional (1D) nanostructures are attracting a great deal of attention due to their essential role in developing understanding of the fundamental concepts of quantum confinement effects [43]. Their applications, however, extend beyond this to nearly all scientific research fields including biomedicine [44], biomaterials [45], microscope probe tips [46], nanoelectronics [47] and energy related materials [48]. While carbon nanotubes (CNTs) are the most studied nanotubes of other materials have been investigated for targeted applications [49]. For example, several researchers have indicated the potential benefits of perovskite nanotubes for application in ferroelectronics [50], lithium-air batteries [51] and, of relevance to this chapter, solid oxide fuel cells (SOFCs) [9].

3.1. Synthesis

Several techniques have been employed for the synthesis of perovskite nanotubes, which can be divided into template-free and template-based methods. The former involves several synthesis routes such as hydrothermal [52,53], solvothermal [54], electrospinning [55] and sonochemical [56] which allow production of 1D oxide nanostructures. Due to the complexity of producing nanotubes with perovskite structure, only the hydrothermal route has yet led to high quality, reproducible 1D perovskite nanostructures. This technique typically allows production of nanotubes/wires with small diameters (~10 nm) [57] which reduces their suitability for SOFC application, as smaller nanotubes are more prone to sinter at operating temperature [58,59]. Their scalability to large-scale production is also considered an important limitation. Template assisted routes therefore emerge as the best option to produce perovskite nanotubes with suitable dimensions, as size, shape and structural properties of the final product can be easily controlled by the use of suitable templates. In addition, using a precursor solution allows tailoring of properties through manipulation of composition, even allowing the use of composites. Two types of template membranes are commonly used: anodized aluminium oxide (AAO) and polymeric membranes.

3.1.1. Anodized aluminium oxide (AAO) membranes

AAO membranes are produced by anodic oxidation of aluminium sheets in solutions of sulphuric, oxalic or phosphoric acids. They exhibit uniform and parallel pores with sizes ranging from 10 nm to 100 μm and densities as high as \(10^{11}\) pores cm\(^{-2}\). The most common route consists of filling the membranes pores with a suitable precursor solution which is then heat treated to form the perovskite material, and subsequently separated from the template by etching the membrane away. Nevertheless, other techniques such as pulsed laser deposition [60], chemical vapour deposition [61] and electrodeposition have also been employed for this purpose [62]. The main advantage of these membranes is their rigidity and stability at high temperatures, maintaining the desired dimensions throughout the thermal treatment required to achieve the crystalline phase. The complete removal of the template after nanotube growth remains challenging. In order to overcome this limitation, polymeric membranes are considered a suitable alternative, facilitating their removal by thermal treatments.

3.1.2. Polymeric membranes

The commonly employed polymeric templates consist of polycarbonate membranes with pore diameters ranging from 100 nm to several micrometres. In this case the pores are also filled with a precursor solution and heat treated to obtain both the desired crystalline phase and removal of the polymeric template. Despite the temperature mismatch between the membrane removal (~ 300 °C) and phase formation (> 600 °C), promising results have been obtained using this technique for the production of perovskite nanotubes with a range of dimensions. In addition, it is worth noting that these membranes are low-priced when compared to the AAO ones.
3.2. Properties
As previously discussed, the use of membranes allows production of 1D nanostructures with a large range of compositions, leading to high electrochemical performances [58,59,63]. The production of composites has also lead to improved ionic conductivity and thermomechanical compatibility [64,65]. In addition to the versatility achieved through compositional manipulation, the electrochemical performance is also influenced by the high surface area to volume ratio that these materials present. This high surface area, 5 times that of bulk materials, increases the active TPB and results in high electrochemical performance. These nanostructures also show better resistance to sintering in comparison with nanoparticulated electrodes, especially when greater than 100 nm in diameter. As the electrochemical response of the 1D perovskite nanotubes is measured as a full 3D nanomaterial, its detailed analysis will be discussed in the relevant section.

![Fig. 2 1D perovskite nanostructures with different dimensions](image)

4. 2D Nanomaterials
A unique aspect of nanomaterials is their high surface area to volume ratio, particularly high in those in 2D, which results in a higher reactivity, making them suited to adsorption and catalysis applications. Another significant advantage of nanomaterials is their ability to change their fundamental properties such as magnetization, optical properties, melting temperature, etc. with respect to micro and macroscopic materials. Some of these properties are directly related to surface interactions between nanoparticles (eg. hardness or melting temperature) but the electronic properties are controlled by so-called "quantum confinement effects". This effect does not come into play when moving from micro to macro dimensions, but becomes dominant when the nanometer size range is reached.

4.1 Thin Films
A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness and are often synthesised from a gas phase [66,67]. Physical-chemical techniques for thin film preparation include:

- Hot dipping
- Soldering enamel and ceramic
- Physical vapour deposition (PVD) and chemical vapour deposition (CVD)
- Chemical and electrochemical methods
- Superficial treatments such as ion implantation

Among these, vapour phase deposition has seen the most interest in recent years. They are used in a variety of technological processes and are gradually replacing more traditional thin-film deposition techniques. It is possible to synthesize a wide range of materials, both ceramic and refractory thanks to the high processing temperatures. In the SOFC field the most common techniques are pulsed laser deposition (PLD) and CVD. The fabrication of micro solid oxide fuel cells (µSOFCs) is an emerging and highly active field of research that is attracting a great deal of attention in recent years [68,69]. Highly efficient µSOFC power systems are expected to be deployed in a number of applications such as portable consumer electronics devices [70]. These techniques have been employed in the manufacture of nanostructured thin-film electrolytes (10-200 microns thick) due to a reduction in electrical losses and lower sintering temperatures [71-75]. In the case of laser ablation, it is possible to obtain nanomaterial with virtually any composition and by controlling working conditions materials with vertically aligned nanochannels (VANCs), similar to those presented in Figure 3, can be fabricated [76]. These VANCs wholly or partially release the thermal stress generated in the interior as well as that caused by the mismatch in lattice and thermal coefficient of the substrate and the film. The nanochannels extend through the thickness of the layer from the surface to the interface with the substrate. This also
promotes the creation of additional vertically aligned grain boundaries and nanopores which dramatically increases the amount of triple-phase boundary (TPB). Thus, the gas diffusion through the layer is improved, as path tortuosity is reduced, improving the kinetic performance. The first application of PLD as a deposition technique for cathodes in SOFCs was published in 1996 [77]. In this work, Coccia et al. presented the growth of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO), $\text{La}_0.7\text{Sr}_0.3\text{Co}^{111}_{111}$ and $\text{La}_0.7\text{Sr}_0.3\text{Co}^{215}_{215}$ thin films by PLD. They demonstrated that PLD is a suitable technique for the growth of novel materials for SOFC application. PLD has recently been used to fabricate $\text{La}_x\text{Sr}_x\text{Co}-\text{O}$ (LSCO) thin films for SOFC applications, as using integrated oxide thin films for fuel cell design can reduce cell size and cost [78-84]. In the past decade, several materials have been produced by this technique, thereby optimizing the parameters for obtaining thin films for potential application as SOFC cathodes. It has thus been possible to establish the relationship between deposition temperature and thin film morphology and the influence of substrate type on preferential material growth [76,85-87]. Utilizing PLD it has been possible to fabricate an entire thin-film-based SOFC composed of a thin-film electrolyte grown on a nickel foil substrate and a thin-film cathode ($\text{La}_0.5\text{Sr}_0.5\text{CoO}_3$ - LSCO) deposited on the YSZ electrolyte obtaining a maximum output power density of ~110 mW/cm$^2$ in the 480–570 °C temperature range [81].

![SEM images](image)

**Fig. 3** SEM images of the surface (a) and cross section (b) of the $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ films on polycrystalline YSZ substrates. Samples deposited at 700ºC exhibit a high roughness and pyramidal surface grains. The cross section images show columnar growth.

Among vapour deposition techniques, the most widely used is chemical vapor deposition (CVD) in which the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired thin film. The CVD technique reached its peak in the early 1970s due to the advantages of its application in the microelectronics field. Currently, a wide range of materials can be deposited by this technique: elemental materials such as C, Si and Ge, binary (oxides, nitrides, silicides) and ternary compounds. CVD is one of the most common techniques used for the growth of carbon nanotubes [88] which find, amongst others, application as porosity templates for SOFC cathodes, as discussed later. As with PLD, CVD has been mainly used to produce dense electrolyte films, 1-10 microns thick, on dense and porous substrates [89-91]. CVD has been employed to obtain thin films of perovskite-structured materials for application in SOFC, for example the work of Meng et al. which employed a novel, aerosol assisted technique to obtain films such as LSM [92]. Abrutis et al. have also produced manganite, ferrate and gallate films using this technique to study their electrochemical behaviour for application as oxygen permeation membranes [93]. This technique has also allowed the production of nanostructured composite cathodes (manganite:coaltarite: gadolinia doped ceria), graded in both composition and microstructure [94]. In this study there is a significant reduction in interfacial ohmic resistance, giving rise to energy densities of 480 mW/cm$^2$ at 800 °C. It has also been possible to obtain 3D heterostructured electrodes by depositing iron oxide on a porous $\text{SrSc}_{0.2}\text{Co}_0.8\text{O}_{1.8}$ (SSC) perovskite [95]. A uniform distribution of iron catalyst onto the electrode has been achieved which promoted the ORR at the cathode and gave ohmic resistances as low as 0.01 Ω cm$^2$ at 700 °C. This composite electrode has been tested at 650 °C for 250 h without observing the appearance of any degradation, something that was not possible using Pt as catalyst.

### 5. 3D Nanomaterials

There are two types of materials which can be included in the 3D nanostructures category. First, those whose dimensions are above the 100 nm limit but present characteristics which can be associated with certain features on the nanoscale, such as the porosity (pores < 100 nm). Other materials included in this group are the 3D materials formed by 0-, 1- or 2D nanostructures. 0- and 1D nanostructures cannot be considered for practical SOFC applications however 3D nanostructured materials are expected to exhibit interesting improvements, as reported by Adler et al. [96].
5.1 Meso- and macroporous materials

The most common 3D nanostructures are macro and mesoporous materials, in which pore formation is controlled. These pores can be randomly distributed throughout the cathode or highly ordered in three dimensions. The most common materials employed as pore formers consist of polymethylmethacrylate polymeric microspheres (PMMA), polystyrene (PS) [97]. These microspheres are mixed with the cathode precursor solution and then removed by heat treatment and the desired crystalline phase formed. The pore diameters vary depending on microsphere size and synthesis temperature, leading to mesoporous materials with pore diameters between 2-50 nm or macroporous materials with pore diameters greater than 50 nm. The generated pores will result in greater surface area in contact with the gas, promoting the adsorption of oxygen in cathode application. Not only is the generation of a large number of small pores important, but also their interconnection to facilitate gas flow [98,99]. It has been shown that the use of macroporous structures (1.85 μm pore diameter) with a porosity of about 60% reduces the interfacial polarization of purely electronically conducting materials such as LSM, obtaining a higher performance cell [100]. Similar results were obtained by Pinedo et al. using three different types of microspheres (PMMA, PS and PC), observing improved cathode performance with decreasing pore size and increasing TPB [101]. Ruiz-Morales et al. have also achieved a significant improvement in electrochemical performance of LSCM / YSZ composites in symmetrical cells through structural optimization [102]. The ordered areas are, however, restricted to a few millimetres due to cracks produced during the shrinkage of the structure template removal. In some cases, the microstructure is very likely to collapse during fabrication or in operating conditions in an SOFC due to particle growth at intermediate temperatures [9].

5.2 Materials with vertically aligned nanochannels (VANCs)

One interesting approach is the creation of nanochannels for which vertically aligned carbon nanotubes (VACNTs) are considered the best templating material [103]. Carbon nanotubes present an important advantage with respect to the polymeric templates mentioned in the previous section, as they are thermally stable up to temperatures around 650 ºC. As the required temperature to obtain the crystalline phase is often around 700ºC, the nanometric channels are formed at the end of the thermal treatment significantly reducing the free evolution of the microstructure and avoiding problems observed with polymeric microspheres. VACNTs are primarily synthesized by chemical vapour deposition. More detailed information about their synthesis and properties has been reported by Leonhardt et al. [104].
Non-aligned CNTs find potential application in creating composites with the perovskite electrode material [105,106] and in controlling grain size [107], but these still present a large number of limitations for long term application in SOFC devices, and therefore are out of the scope of this chapter.

6. Electrochemical response

A great deal of effort has been invested in lowering the operating temperature to the intermediate temperature range of SOFCs, without affecting cathode polarization. The study carried out by Adler et al. set the basis for the search for new materials and the optimization those already known. As they stated, the characteristic active width for the ORRs in porous MIEC electrodes is limited by the oxygen surface exchange and solid state diffusion [96]. Consequently, the oxygen self-diffusion coefficient ($D^*$) and surface exchange rate ($k^*$) must also be considered in order to look for suitable electrode materials [108]. Tarancón et al. [109] and Chroneos et al. [110], reported the low activation energy for oxygen reduction in double perovskites, which convert them into suitable candidates for operation at reduced temperatures [5,6]. Equations 1-3 detail the complex contributions to cathode resistance ($R_{chem}$) and time constant ($t_{chem}$) [96].

$$R_{chem} = \left[\frac{RT}{2F^2}\right] \cdot \frac{\tau_s \cdot \gamma_{TD}^2}{(1-\varepsilon) \cdot a_s \cdot c_{mc}^2 \cdot k^\delta \cdot D^\delta}$$ (1)

$$t_{chem} = \frac{(1-\varepsilon)}{a_s} \cdot \frac{c_0}{c_{mc}} \cdot \frac{1}{k^\delta}$$ (2)

$$\frac{c_0}{c_{mc}} = \frac{3-\delta}{3}$$ (3)

Where $\varepsilon$ is the porosity, $a_s$ is the electrochemical active surface area, $\tau_s$ is the tortuosity, $c_{mc}$ is the concentration of oxygen lattice sites, $k^\delta$ and $D^\delta$ are the chemical surface exchange and chemical diffusion coefficient, respectively. $C_0$ is the concentration of oxygen ions, $\delta$ the fraction of oxygen vacancies and $\gamma_{TD}$ is the so called thermodynamic enhancement factor defined as $\frac{1}{2}(\delta lnpO_2)/(\delta lncO)$.

These equations show that not only do the oxygen self-diffusion and surface exchange coefficients appear as factors for the ORR, but the level of porosity and surface tortuosity also play important roles. The optimization of the microstructure to develop electrodes with higher surface areas and suitable porosities is an essential step to be considered, alongside material development. The creation of 0-, 1-, 2- and 3D nanostructures therefore emerges as a promising route to create high-performance electrodes with a highly expanded surface area.

7. Summary

In this chapter a range of perovskite type nanostructures are described, these include nanoporous materials, nanocomposites, nanotubes, nanoparticles and thin films, which have shown promising properties for their use as cathode materials in SOFCs. The decrease to the nanoscale range is seen to promote not only the increase of active area for the reduction of oxygen, but also allows the tailoring of electrode properties. As the electrochemical and thermomechanical properties observed in bulk materials are also kept in the nanomaterials, the electrochemical performance of the latest is usually higher than the bulk. In addition, the importance of these nanostructures is expected to increase with the reduction of operating temperatures as limitations ascribed to sintering processes become reduced. According to this fact, the nanotechnology is thought to play an important role for the creation of new materials and the optimization of the already known ones, promoting significant advances on the development of this environmental friendly technology.

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