Catalysis Today 146 (2009) 367–377

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Preparation and characterization of catalyst thin films

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ARTICLE INFO

Article history:
Available online 4 July 2009

Keywords:
Electrocatalyst thin films
EPOC
Porous structure
Electrode materials
Electrolyte materials

ABSTRACT

Many devices used in catalysis are based on high surface area materials in which catalytic reactions are carried out inside pores, channels and other confined cavities for which the deposition of catalyst thin films is required. This paper provides an overview of the methods in use for the preparation and characterization of catalyst thin films, and focuses more specifically on thin films involved in the electropromotion of catalysis (EPOC). In fact, EPOC or NEMCA (Non-Faradic Electrochemical Modification of Catalytic Activity) have shown the importance of being able to combine electrical contacts between catalytic metals and ion conducting oxide layers as well as to develop in the same system catalytic materials with large specific surface area. The different aspects of thin film preparation and characterization are described in relation to catalyst thin films deposition. Multimodal and hierarchic porous structures can be obtained from the assembly of catalyst thin films with various carrier materials, anticipating more efficient catalytic systems. Chemical and physical coating techniques are compared with a special attention on those useful for the preparation of thin films with controlled porous structure and morphology. With regard to EPOC systems, electrode and electrolyte materials of interest for electrochemical catalytic devices are listed and typical examples of systems based on electrocatalyst thin films are given.

1. Introduction

One of the main objectives of catalysis research is to design and tune activity and selectivity of catalysts by controlling their structural properties at the atomic level. Another important aspect, particularly in the case of heterogeneous catalysis, is the way in which catalyst materials are implemented into catalytic reactors. For example, this is the case of multifunctional reactors capable of carrying out together with chemical reaction other functions like mixing, heat exchange, separation and other additional functionalities. In this regard microchannel reactors have significant advantages over packed bed reactors, including faster heat and mass transfer, which allow for process miniaturization without loss of throughput. In other respects, many catalytic devices used in environmental catalysis are based on monolithic supports in which catalytic reactions occur in channels, porous walls and other confined cavities for which coating of catalyst thin films is required. Other catalysts films are prepared in such a way that it combines several functionalities, for example photocatalytic activity and wettability (superhydrophilicity or superhydrophobicity). Moreover, for application like self-cleaning glass panels, they must be optically transparent and deposited on large flat surfaces.

For all these devices, thin oxide films as designable catalysts and catalyst supports are of utmost importance to control the functional characteristics and, thus their intrinsic catalytic properties or the properties of the catalytic species deposited onto them. Several challenges can be mentioned in relation to the development of these catalyst thin films. Originally, they afford the opportunity to really surpass the limitations of the conventional catalyst carriers in terms of thickness, surface area, control of porosity and catalyst accessibility. They can also take advantage of the new generation of microporous and mesoporous solid materials for the preparation of supported catalyst layers able to exhibit high surface area and hierarchic porosity. Another role of catalyst thin films processing should be to promote microreactor technology by a progress in techniques to incorporate very active catalytic materials in micro-structured devices.

In other respects, electrocatalysis is a field in which catalyst thin films are essential for providing both electrochemical and catalytic efficiency. Moreover the latest developments of concepts such as NEMCA (Non-Faradic Electrochemical Modification of Catalytic Activity) or EPOC (Electrochemical Promotion of Catalysis) have shown the importance of being able to combine electrical contacts between catalytic metals and ion conducting oxide layers as well as to develop in the same system catalytic materials with large

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doi:10.1016/j.cattod.2009.05.012

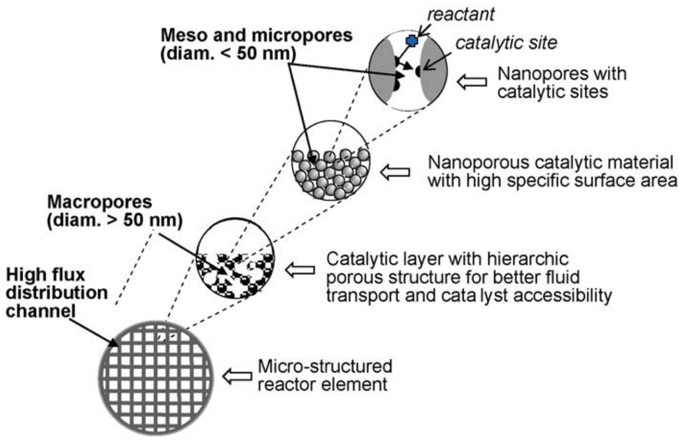

Fig. 1. Design of a catalytic systems based on a multimodal and hierarchic porosity.

specific surface area. The aim of this review is to bring out and illustrate promising pathways for preparing and characterising catalyst thin films with controlled porous structure and morphology. Different strategies are presented with special attention on those well adapted to electrocatalyst thin films.

2. Materials design for catalyst thin films

2.1. Concepts of multimodal and hierarchic porosity

Usually, the characteristics of porous structures are described according to the IUPAC pores classification. Macropores are defined as pores larger than 50 nm, mesopores are typically in the range of 50–2 nm in size whereas micropores correspond to pores smaller than 2 nm. Beyond the pore size difference, the aforementioned classes of pores also differ in terms of geometric factor, mass transport mechanism inside the porosity and other specific properties related to the inner pore surface characteristics. The combination of different porosity levels in a same material can afford the possibility of new designs for catalytic systems. The different structural levels involved in the design of catalytic systems with multimodal and hierarchic porosity are schematized in Fig. 1. For example, micro-structured reactor elements are typical catalytic systems in which better fluid transport efficiency and catalyst accessibility are expected [1]. For that, the catalytic materials in these systems are implemented as catalyst thin films in which porosity generates both a high specific surface area and highly dispersed and accessible catalytic sites [2].

Each porosity level has a specific role in regard to the transport of reactants and the completion of reactions on catalytic sites. Typically macropores display a mass transfer based on viscous flow and are very efficient for reactant distribution through the catalyst carrier. In other respects a mesoporous structure is of prime importance for the catalytic material itself. Effectively, mesopores are perfectly suited to promote contact between gaseous molecules and catalytic sites thank to Knudsen diffusion mechanism. Finally microporous structures hold specific interest in the case of selective catalysts in which a size effect is expected like in zeolites or in membrane reactors in which microporous layers are used as selective barrier for products extraction [3]. Typically, the control of porosity in supported catalyst thin films extends over macro, meso and micropore ranges involving in some cases the porosity of the carrier material itself. An insight into carrier materials of interest for catalyst thin film implementation is presented hereafter.

2.2. Structured material based supports for catalyst thin films

Honeycomb structures, micro-structured reactors or simple macroporous pellets are as many designs for catalytic devices in which supported thin films can be implemented in view of catalytic application. Different hollow and porous materials structures are available in the form of fiber mats, foams, macro and mesoporous structured materials made of ceramic, glass, metal or polymer, Fig. 2. In fact, the choice of a catalyst carrier, independently of the carrier shape, depends on many parameters related to the type of reaction, the reaction media, the operating pressure and temperature, the fluids hydrodynamic and to other additional technical and cost factors. Finally, efficient and

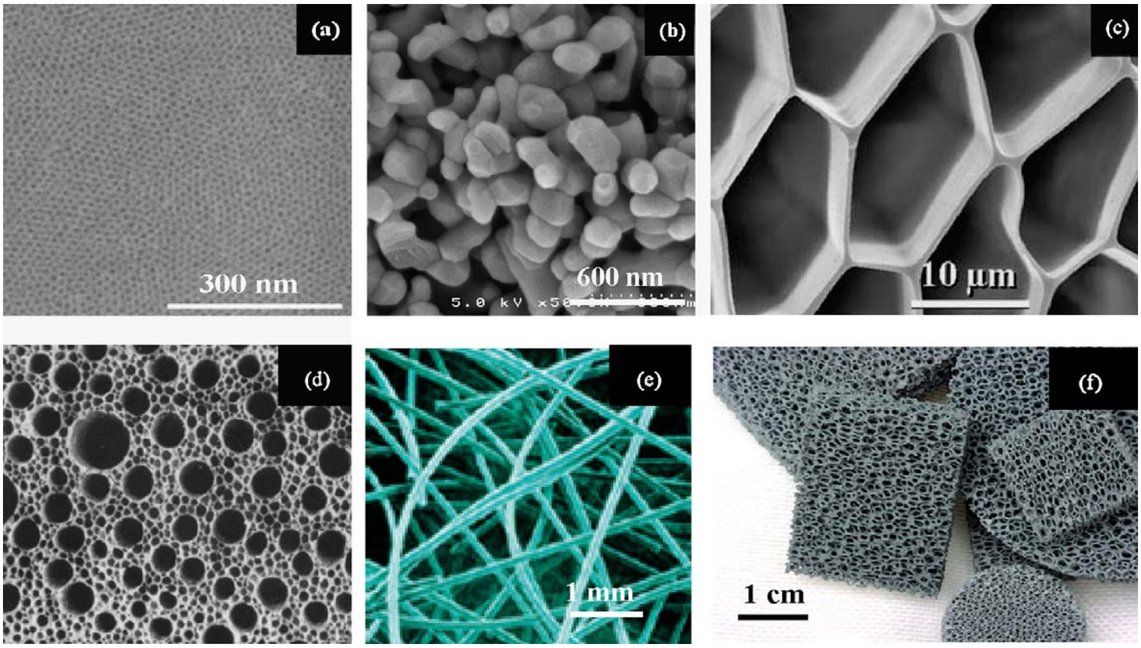

Fig. 2. Different porous structures of materials usable as catalyst carriers. (a) Ordered mesoporous solid; (b) macroporous grained solid; (c) micro-structured material; (d) cellular material; (e) fibrous non-woven material; (f) foamed material.

intelligent reactor designs must be utilized to make a catalytic reactor industrially and commercially attractive.

Compared to a classical chemical reactor, an electrochemically promoted chemical reactor differs in design and nature of materials. Accordingly, specific requirements come out for carrier materials due to the need to operate transport of charged species (ions, electrons). Most often in electrocatalysis and more specifically in electropromotion of catalysis, ionic and electronic conductors are coupled to selective catalytic metals on which charged species migrate and modify catalytic behaviour. Firstly, an efficient electrocatalyst device requires the use of thin catalyst electrodes with high dispersion, then an efficient current collection must be achieved through interconnects. An example of an electrochemically promoted reactor with a novel monolithic design is described in [4]. The structure of this reactor is presented in Fig. 11.

3. Electrocatalyst materials

Actually, Electrochemical Promotion of Catalysis (EPOC) is not limited to any specific type of catalytic reaction, metal catalyst or solid electrolyte. In fact EPOC bears several similarities with heterogeneous catalysis, fuel cells and electrolysis so that it is suitable to describe electrocatalyst materials in terms of electrode and electrolyte materials. Furthermore, in order to make these materials suitable for practical use, most of them have to be developed as catalyst thin films.

3.1. Catalytic electrodes

Catalytic electrodes can be classified into three categories: metallic electrodes, ceramic electrodes or cermets electrodes. The noble metal mostly used as electrode is platinum, which can be used for combustion of propane [5], for electrochemical reduction of nitric oxide in presence of excess oxygen [6], or for electrochemical hydrogen pumps for hydrogen separation with a pure protonic conduction electrolyte [7]. The use of Pt, Pd, Rh, Ag, Ni, and Au as catalytic electrodes has been reported for more than 50 catalytic reactions which are promoted electrochemically. For example, rhodium, palladium can be used for ethylene oxidation, silver or gold for carbon monoxide oxidation. Copper-based catalysts are known to be effective for methanol synthesis and it can be used as working electrodes for the hydrogenation of carbon dioxide [8]. However, pure metallic electrodes suffer deterioration due to the formation of adsorbed poison species. For example Pt is an excellent catalyst for dehydrogenation of small organic molecules (such as methanol) but it is extremely susceptible to poisoning by CO. The incorporation of CO-catalysts such as Ru, Sn, Au, Rh, Pd, into the Pt catalysts have been studied to minimize the poisoning effect of CO. Platinum/ruthenium alloys present the best results. Pt–Sn/C bimetallic catalysts may function as a methanol-tolerant cathode catalyst in a direct methanol fuel cell [9].

Ceramic cathode and anode, used in SOFC, need high electrocatalytic activity for oxygen reduction and for hydrogen oxidation respectively. The most widely used cathodes for SOFC are $(La_{1-x}Sr_x)_{1-y}MnO_{3\pm\delta}$ with $x = 0.10–0.30$ and $y = 0–0.20$. A number of cathodes, derived from the highly catalytic active Sr^{2+} doped $LaM'O_{3-\delta}$ (M′ = Co, Fe or Ni), has already been investigated, which present mixed ionic and electronic conductivity. $La_{0.75}Sr_{0.25}Mn_{0.95-x}Co_xNi_{0.05}O_{3+\delta}$ $(0.1 < x < 0.3)$ is one example published recently in the literature for a cathode application in IT-SOFC [10]. $Sm_{0.5}Sr_{0.5}CoO_3$ cathodes were studied for low-temperature SOFCs. A family of oxides with K_2NiF_4-type structure and which have a general formulation $A_2MO_{4+\delta}$ with M a transition metal cation and A, a lanthanide or alkaline earth, has been studied for a few years. Due to their excellent mixed ionic and electronic conducting properties and because they exhibit high oxygen bulk diffusion and surface exchange coefficients, these nickelate materials are being promoted in SOFC application domain [11]. A lot of composite cathodes are studied, such as LSM/YSZ, where an ionic and electronic conductor are mixed [12], or such as $Sm_{0.2}Ce_{0.8}O_{1.9}$ with a nano-network of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ [13], to enhance the density of ‘‘triple phase boundary’’. The ceramic–metal composites of YSZ and Ni, where the metallic phase combines the functions of electronic conductor and catalyst, are the commonly used anode of SOFC. YSZ prevent sintering of Ni particles, enlarge the active reaction zone. Nickel is an excellent catalyst for both steam reforming and hydrogen cracking but suffers from carbon deposition and sulphur poisoning when hydrocarbon fuels are used. A lot of anode materials are studied to solve the problem of carbon deposit when hydrocarbon fuels are used. Attention was drawn to the electrodes based on metallic copper such as Cu–YSZ or (Cu, Ni) alloy–YSZ cermets, which decrease coking in CH_4 containing atmospheres. However, the electrochemical performance of these anodes is lower than that of Ni–YSZ cermets. To enhance the activity of conventional anode cermets some researchers incorporate a catalytically active phase based on CeO_2 which exhibits mixed ionic and electronic conductivity in a reducing atmosphere due to reduction of Ce^{4+} to Ce^{3+}. Thus a Ru–Ni–$Ce_{0.9}Gd_{0.1}O_{1.95}$ anode that was directly operated on hydrocarbons at 600 °C is suggested to be the suitable anode for low-temperature SOFCs [14]. Recently, a lot of new compounds with perovskite structure have been offered as alternative anode materials in SOFC. It has been shown that $La_{0.5}Sr_{0.5}TiO_3$ demonstrates good ionic conductivity and could be used as a basic phase for producing composite anodes for SOFC [15]. Cermets are studied for cathode material also, for example Ag/$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ [16] cathode for IT-SOFC where Ag can greatly improve the catalytic activity.

3.2. Solid electrolytes

Zirconia-based electrolytes, such as yttria-stabilised-ZrO_2 (YSZ), are the most popular solid electrolytes. It is used as the electrolyte in SOFCs because of its attractive ionic conductivity, stability in both oxidizing and reducing environments, and compatibility with the electrode materials [17]. A promising, although less widely used, is the scandium stabilized zirconia phase, which has a higher conductivity than YSZ in the temperatures of interest for SOFCs. The Gd doped ceria (CGO) are known to be good oxygen ion conductors with applications in solid oxide fuel cells (SOFCs), oxygen sensors, oxygen pump and in methane to syngas conversions [18]. As compared to zirconia, ceria has a higher conductivity, particularly at low temperatures, and a lower polarization resistance [19]. The primary disadvantage of ceria is its electronic conduction at low oxygen partial pressures [20]. The perovskite, $LaGaO_3$, can be doped with strontium and magnesium, $La_{1-x}Sr_xGa_{1-y}Mg_yO_3$ (LSGM), to produce a material with good low-temperature oxygen-ion conductivity. The conductivity of LSGM is higher than those of YSZ and ScSZ and similar to or lower than that of CGO. Moreover, LSGM does not have an easily reducible ion, like Ce^{4+}, and thus is superior to CGO for use in low oxygen partial pressures.

Perovskite oxides based on $BaCeO_3$, $SrCeO_3$, $CaZrO_3$ and $BaZrO_3$ demonstrate good proton conduction under hydrogen-containing atmosphere between 300 and 1000 °C. $BaCeO_3$-based proton conductors show the highest conductivity but suffer from poor chemical stability. Zirconate-based proton conductors are relatively more stable but have lower conductivity. A solid solution between $BaCeO_3$ and $BaZrO_3$ show a good balance between protonic conductivity and chemical stability [21]. Na-β”-Al_2O_3 is used as a solid electrolyte to study the effect of sodium promoters for the selective catalytic reduction of NO by propene [22]. It has been shown that the electrochemical promotion by potassium of Pt/K-βAl_2O_3 catalyst for low-temperature propene combustion was very efficient both near-stoichiometric and oxygen-rich conditions [23].

Polymer electrolytes and related electrodes are also of interest as electrocatalyst materials. Polyperfluorosulfonic acid polymer electrolyte under trademark of Nafion® (DuPont) is most commonly used as polymer electrolyte membrane. Polybenzimidazole (PBI)-H_3PO_4 is an interesting electrolyte because it is stable at temperatures higher then 100 °C, at which CO poisoning of the Pt catalyst is of little importance. For example, NO can be electrochemically reduced without any reducing agent (like CH_4), in the (NO,Ar) Pt/C|PBI–H_3PO_4|Pt/C, (H_2,Ar) fuel cell with participation of H^+ or electrochemically produced hydrogen [24].

4. Preparation and characterization of catalyst thin films

4.1. Methods for the preparation of supported thin films

There are several chemical and physical pathways capable of yielding effective catalyst thin films. However, appropriate coating techniques have to be selected in relation to the characteristics of catalytic devices in which thin active layers have to be implemented. Moreover the microstructure and the porosity of the film are strongly related to the technique used for deposition which can be carried out either in wet medium, in a vapour or gas phase or in vacuum. In the case of a wet chemical method the film microstructure is largely influenced by the size of starting particles or colloids, the rheology of the suspension and the elimination of the solvent. On the other hand, chemical vapour deposition is based on the physical decomposition of molecular precursors contained in a gas phase. In the last case the microstructure of the layer is mainly determined by the decomposition mode (thermal, plasma, microwave, etc.) and to a less extent by the nature of the precursors. Finally, for a physical method, the microstructure results from the growth process of the film in relation with the physical parameters of the process. Examples of chemical or physical methods used for thin solid films deposition are given hereafter which can be suitably adapted to the case of electrocatalyst thin films.

Chemical routes based on wet processes can be advantageously applied to the deposition of thin layers. They specifically allow the preparation of mesoporous structures with a high specific surface area, well adapted to catalytic application. Usually these methods can be carried out in a very simple way and are cost-effective in view of an industrial development. The sol–gel process is undeniably the most studied chemical method to prepare nanostructured materials and thin films [25]. Usually, thin and homogeneous supported layers can be obtained by spin-coating or dip-coating [26–28] techniques. In the case of hollow or porous structures in which the walls have to be covered with an active layer thin enough to prevent channel or pore blocking, the slip-casting technique coupled with the sol–gel process can be advantageously used. One of the specific features of sol–gel chemistry is the possibility to create ordered mesoporous structures with very large specific surface area. For that, besides basic components (inorganic precursors, hydrolysis catalysts and solvent), a structure directing chemical agent is introduced as specific additive at the sol stage. Its role is to generate a template effect during gel formation. Surfactant molecules and their self-assembling properties were used first by the Mobil Oil Corporation to obtain ordered mesoporous, powder-like silica material [29]. Later on, this method was adapted to the preparation of continuous ordered mesoporous films. In this case, the rapid vaporization of solvent and water during the coating process generates an increase in the concentration of the surfactant and precursor and an acceleration of the sol–gel process. During concentration, the aggregation of the surfactant molecules creates micelles which in turn form liquid crystals. Finally, the liquid crystal phase acts as a template during gel formation and leads to the formation of an inorganic framework with an ordered mesoporous structure [30]. Actually, the preparation of mesoporous inorganic films with ordered mesoporosity has been thoroughly studied and additionally to surfactant molecules, an ordering effect has been described with amphiphilic polymers or chelating agent [31]. Mostly studied on silica materials, ordered mesoporous structures are now investigated for a number of metal oxides offering specific interest in catalysis. For example porous alumina thin layers were prepared using a mesophase templating method [32]. In a recent publication [33] the preparation of mesoporous alumina thin films was described from the combination of an inexpensive and commercially available copolymer with aluminium chloride or nitrate (salts), using an EtOH–surfactant–NH_3–H_2O–salts system and the aforementioned evaporation-induced self-assembly method. TiO_2 is another important metal oxide used as thin coatings in fuel cells, as electrodes in electrochemistry and electrocatalysis, in electro-optics and in photocatalysis. An example of preparation of mesostructured anatase thin films using the mesophase templating method is given in [34].

By comparison with the sol–gel process, there are wet chemical methods based on aqueous suspensions of submicronic particles or solutions of metal cations containing pore formers which can be used directly for the preparation of porous microstructures. Usually the mean pore size obtained by this method is in the macroporous range [35]. It has been recently applied to metal oxide materials of interest for SOFC, in particular for electrode design [36]. The method uses aqueous stoichiometric cation solutions of metal nitrates, citric acid as complexing agent and PMMA microspheres as pore former. Ferrite and manganite cathode materials, e.g. $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ (LSF) and $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM), anode materials $La_4Sr_8Ti_{11}Mn_{0.5}Ga_{0.5}O_{38-\delta}$ (LSTMG) and NiO–YSZ composites were prepared using this approach. In this area, the spray pyrolysis method is a very versatile coating process, able to use either liquid solutions or sols as starting materials. It has been widely applied for the deposition of oxide thin films, in particular for the preparation of SOFC and catalyst thin films. Related examples are the synthesis of $Gd_{0.1}Ce_{0.9}O_{1.95}$ thin films [37], zirconia-based coatings [38], composite lanthanum manganite/yttria-stabilized-zirconia films [39] and the deposition of Pt/YSZ electrochemical catalysts for selective catalytic reduction of NO by C_3H_6 [40].

Electro-based techniques like electrolytic or electrophoretic deposition as well as electroless deposition are other wet processes of interest for the preparation of thin films but with less flexibility in the design of controlled porous structures. In fact electro and electroless techniques are more desirable for the synthesis of particulate thin catalyst films whereas the electrophoretic process is more versatile and can yield dense or porous coatings. Electrodeposition is well adapted to metallic conductive supports like stainless steel. SS/ZrO_2/Pt and SS/ZrO_2/Cu–Co catalytic materials were prepared by electrolytic deposition with the aim of catalytic oxidation of volatile organic compounds [41]. Electrophoretic deposition is one of the colloidal processes generally used in ceramic production. It displays advantages of short formation time, needs simple apparatus, little restriction of the shape of substrate, no requirement for binder burnout as the green coating contains few or no organics [42–45]. The basic difference between an electrophoretic deposition and an electrolytic deposition is that the former is based on the suspension of charged particles in a solvent whereas the later is based on solution of salts, i.e., ionic species. Depending on the charge, positive or negative, of the particles the process is called either cathodic or anodic electrophoretic deposition. It has been used successfully for a large number of applications, and among others for nanosize zeolite membranes, gas diffusion electrodes and sensors, functionally graded ceramics, layered ceramics. The main intrinsic disadvantage of electrophoretic deposition, compared with other colloidal processes (e.g. dip, spin and slip-casting coating), is that it cannot use water as the liquid medium, because the application of a voltage to water causes the evolution of hydrogen and oxygen gases at the electrodes which could adversely affect the quality of the deposits formed. Otherwise, electroless deposition generally refers to one of two different processes: (1) direct electroless deposition, in which the metal is directly reduced by a reducing agent, or (2) a displacement reaction, in which a more active metal carries the reduction. This technique was used to modify porous semiconductor surfaces with fcc type metals which can in turn be used in catalysis and for electrical contact [46].

Among the chemical methods that are carried out in a gas phase and applied to the production of catalytic structures, a very promising one is the plasma deposition of very thin films from metal-organic precursors supplied to the plasma reactor in a gas carrier phase. More precisely, plasma-enhanced metal-organic chemical vapour deposition (PEMOCVD), has been already used for the preparation of potentially catalytic films such as Pd, Rh, Pt was already mentioned. Recently, it has attracted closer attention provoked by the search for new effective methods for preparing microchannel structures, in which a catalyst in the form of several-nanometer clusters should be uniformly dispersed throughout the microstructure. It is also important that the application of the cold plasma is especially useful for the preparation of supported nano-sized catalysts, because aggregations caused by thermal treatment might be avoided. For example, small particles of CoO_x in the range of 4–6 nm in diameter were deposited in this way on Cr–Al steel carriers and were tested in oxidation of n-hexane [47]. A few other materials with potential catalytic properties, such as thin films of MoOx or TiOx, have been prepared with success by the PEMOCVD method [48,49]. High-power microwave plasma chemical vapour deposition (MPVCD) is another CVD derived deposition method which has been successfully used for a one-step synthesis of a composite C/Pt catalyst thin-film [50]. In this way, simultaneous formation of an electronically conductive carbon support decorated with uniformly distributed ultra-fine (2–4 nm) Pt catalyst led to an efficient electrochemical activity.

Physical vapour deposition includes different deposition processes such as evaporation, sputtering, reactive PVD and pulsed laser deposition (PLD). Evaporation remains the most used method, sputtering results in denser more homogeneous films, reactive PVD needs the addition of gases into the vacuum system, whereas PLD remains an excellent research tool but with no industrial solution. In the last years the sputtering method has gained increasing interest in the field of electrocatalysis as an alternative of the conventional catalysts preparation techniques, particularly for application in the energy conversion electrochemical cells. The sputtered catalysts are usually deposited as thin compact catalytic films directly upon selected substrate materials. The electrochemical behaviour of sputtered films depends essentially on the chosen deposition conditions. It has been shown that by variation of the sputter parameters such as dc- or rf-power, inert and reactive gas flow, partial pressure, temperature, distance between the target and the substrate, it is possible to modify not only the film composition, but also its structure and morphology and thus, to tailor the specific surface and the electrochemical reactivity. There are many examples in the literature of sputter-deposited catalyst films and those dealing with metals (Pt, Rh, Au, etc.) deposition are of particular interest in electrocatalysis. When only the uppermost layers have to be active both for catalysts and electrodes, a deep penetration of the metal into the substrate is unnecessary and then the electrode structures and catalysts can be more easily prepared by direct current sputtering [51]. In the case of radio-frequency (RF) sputtering, the films are generally made up of small crystallites which have developed closely in relation to each other, in such a manner that the pores in between can only be very small. It is then very difficult to precisely characterize the microstructure and the porosity of such films [52]. Typical electrochemical reaction like EPOC of propane combustion [53], CO oxidation [54] or EPOC of NO reduction by C_2H_4 in excess O_2 [55] have been investigated highlighting the influence of the film microstructure on the electropromotion phenomenon. According to [55] there are two main limitations to the commercial development of EPOC, one is the use of expensive thick catalyst films (typically 0.1–5 mm thick) with metal dispersion below 0.01%, the next one is the lack of efficient and compact reactor designs allowing for the utilization of electrochemical promotion with a minimum of electrical connections to the external power supply. Both of these limitations could be overcome via the use of thin sputtered noble metal electrodes with good metal dispersion.

4.2. Characterization methods of electrocatalytic thin films

The characterization of catalyst thin films and specifically of those used in electrocatalysis, requires the combination of morphological, physical and electrochemical techniques in order to afford a comprehensive description, either after preparation or after use, of the coated catalytic layers. With regard to the morphology, not only scanning and transmission electron microscopy (SEM, TEM) but also atomic force microscopy (AFM) can be useful to characterize the crystallite and grain size. However these techniques are not well suited to give quantitative information about open and close porosity. For this reason, physical adsorption isotherms of nitrogen or krypton are sometimes used to determine the surface area of porous thin films, by the Brunauer, Emmet and Teller (BET) method. In practical use this method is quite difficult to carry out because about 1 m^2 of an effective surface is required for the measurement using volumetric techniques. Accordingly the characterization of porous thin film requires specifically adapted methods as it is pointed out later. Other methods like X-ray, Raman, XPS and SIMS are complementary to the previous techniques as they provide information on the structure and the chemical composition of the catalytic material. Finally, electrochemical methods (impedance spectroscopy, voltamperometry/voltametry) are essential to the characterization of the electrochemical properties of electrocatalyst thin films as such.

4.2.1. Morphology characterization methods

Scanning electron microscopy (SEM) is a common technique to determine the microstructure, shape, of electrocatalyst thin films. It can also reveal information on composition of thin films when the SEM is in conjunction with energy dispersive spectroscopy (EDS). The resolution of SEM is determined primarily by the size of the electron spot, which is of the order of 1 to 2 nm on modern instruments. The SEM micrograph shown in Fig. 3 reveals the microstructure of a nano-network of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) manufactured as the cathode for IT-SOFCs [13].

Transmission electron microscope (TEM) can determine the size, shape and arrangement of the particles which make up the thin electrocatalyst, down to the atomic scale. TEM has superior resolution (0.1 nm) than SEM. Crystallographic information and compositional information (combined with energy dispersive spectroscopy) can be determined by using TEM. The TEM technique was used to study the influence of the electrochemical

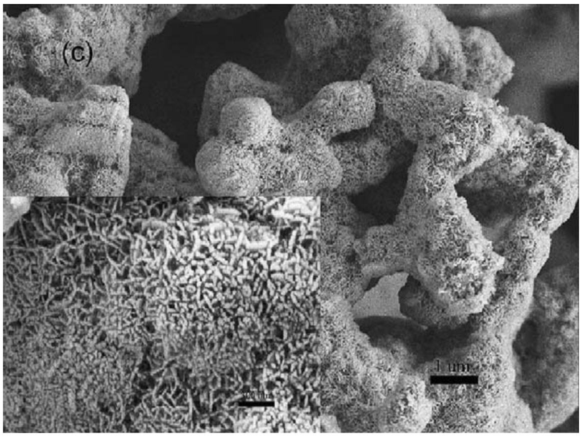

Fig. 3. Cross-sectional microstructures for cathodes frame ($Sm_{0.2}Ce_{0.8}O_{1.9}$) with impregnated $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$, from [13].

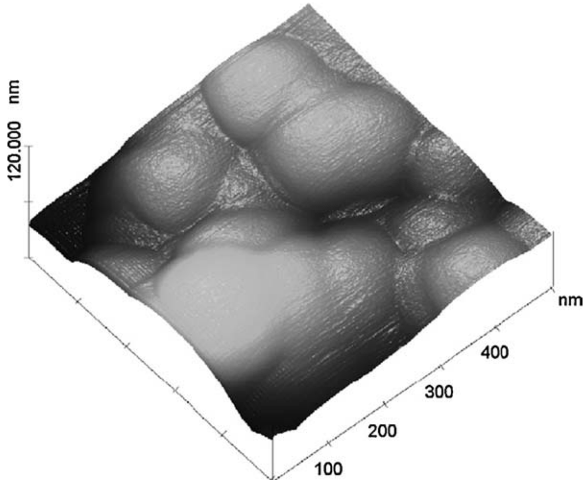

Fig. 5. AFM image at a 500 nm scale of a CGO thin film, from [38].

stressing on the dispersion of Pt nanoparticules in polymer electrolyte membrane fuel cell electrocatalysts, Fig. 4 [56]. TEM can also be used for higher resolution of grain boundary inspection and microstructural analysis of details such as secondary phases that can have a strong influence on the electrocatalytic activity.

The microstructure of surfaces can be investigated with an atomic force microscopy (AFM), which is a very high-resolution (fractions of a nanometer) type of scanning probe microscope. AFM provides a true three-dimensional surface profile compared to an electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample. Fig. 5 gives an example of an AFM image obtained for $Gd_{0.1}Ce_{0.9}O_{1.95}$ thin films [38].

Studying the microstructure of supported thin films but also their behaviour as a function of the environment and their aging entails a thorough characterization of the porous structure. Intrusive methods, like nitrogen adsorption–desorption at 77 K, are well adapted to the study of micro and mesoporosity of bulk materials and powders but become problematic in the case of thin supported films due to the lack of sensitivity when the developed surface area is too small. Alternatively, non-destructive ellipsometry, quartz crystal microbalance (QCM), X-ray reflectometry (XRR), coupled with adsorption–desorption of different vapour probes at room temperature have been mentioned recently as well adapted to characterize microporosity and mesoporosity of supported thin films [57]. These characterization techniques are easy to setup, non-destructive, do not need a special sample preparation and can be easily integrated for in-line characterization in a clean room.

4.2.2. Physicochemical characterization methods

After elaboration or after use in different conditions it is important to study the crystalline or amorphous state of catalyst thin films to make sure that they behave as expected. X-ray diffraction is an essential technique for crystal structure identification and refinement. From the diffraction pattern it is possible to calculate the lattice parameters by Rietveld refinement. Raman spectroscopy can be used to identify the crystalline structure (space group) and to detect possible disordered regions by analyzing the different Raman active modes. The Raman spectroscopy enables the detection of traces lower than 1% in volume, contrary to the diffraction of the X-rays which is limited to a minimum of detection of 5% in volume. For example, Raman spectra of $Pr_2Zr_{2-x}Ce_xO_{7\pm\delta}$ (Fig. 6) show a new band at around 590 cm^{-1} when Ce is introduced at the B site of the lattice ($A_2B_2O_7$) [58].

Secondary ion mass spectrometry (SIMS) is another suitable technique for the composition analysis of thin films. Basically, when a solid sample is sputtered by primary ions of few keV energy, a fraction of the particles emitted from the target is ionized. Thus SIMS consists of analyzing these secondary ions with a mass spectrometer, supplying information about the elemental, isotopic and molecular composition of its uppermost atomic layers. SIMS allows the measurement of many trace elements at very low concentration (ppb-range). During a measurement, the sample is slowly sputtered (eroded) away and that is why SIMS is capable of measuring depth profiles. And since ions of different mass are measured separately, SIMS is ideally suited for the study of isotopic

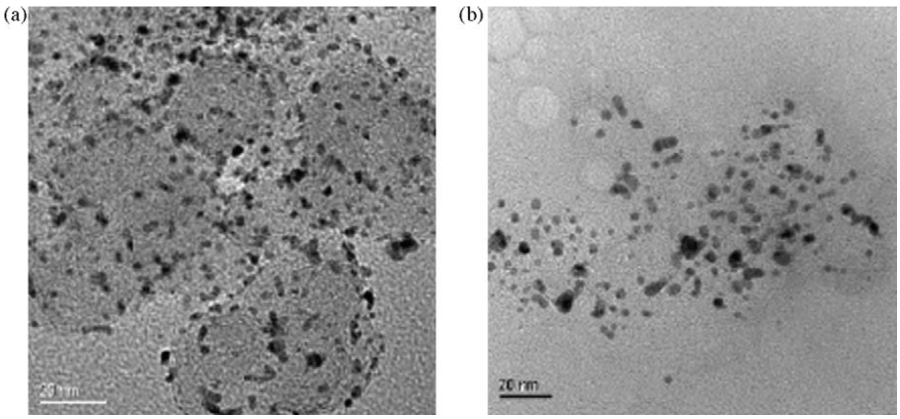

Fig. 4. Representative TEM images of (a) original Pt/C, and the degraded Pt/C under the conditions of potential-static holding at 1.2 V for 120 h, from [56].

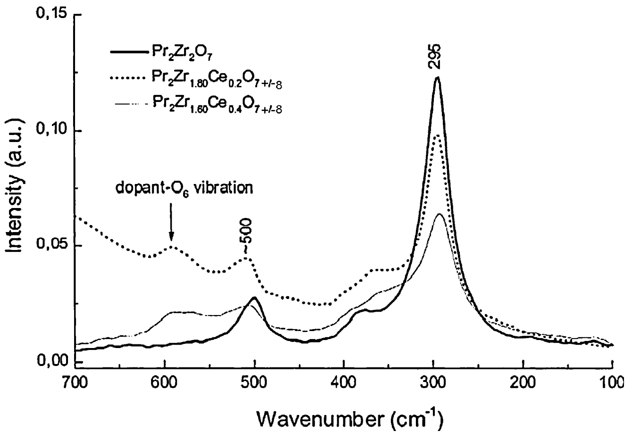

Fig. 6. Raman spectra of Pr_2Zr_{2-x} $Ce_xO_{7\pm\delta}$, $x = 0, 0.2, 0.4$ at room temperature, from [58].

compositions of small samples. So, it has been possible to visualize the oxygen reduction active sites around the O_2/SOFC cathode/electrolyte triple phase boundaries (TPB) by the $^{16}O/^{18}O$ exchange technique and SIMS analysis [59]. In this work, it is proved that the $La_{0.9}Sr_{0.1}MnO_{3-\delta}$ mesh surface is more active for oxygen adsorption or oxygen surface exchange than the YSZ surface, and moreover that ^{18}O can diffuse into the $La_{0.9}Sr_{0.1}MnO_{3-\delta}$ mesh deeper than 20 nm under cathodic polarization.

X-ray photoelectron spectroscopy (XPS) has been already used to determine chemical composition of the catalytic surface thank to the energy determination of the photoelectrons leaving the sample when irradiated with X-ray. XPS allows the metallic species on the oxide surface to be established. It is possible to obtain the abundance of the different species for a metal (different coordination sites or oxidation states) and some information about the nature of the oxygen species on the first layers of the oxide crystallite for example [60].

4.3. Electrochemical (impedance spectroscopy, voltamperometry/voltametry)

Electrical conductors made of electronic and ionic conducting materials play an important role for the implementation of electrocatalytic thin films. Impedance spectroscopy (IS) is a very versatile electrochemical tool to characterize intrinsic electrical properties of any material and its interface. The impedance spectra collected are modelled as an equivalent circuit from which conductivity and capacitance values can be extracted for the bulk, grain boundary, overall electrolyte, charge transfer and electrode conduction components [61].

Cyclic voltammetry enables potentiodynamic electrochemical measurement which is a means to investigate mechanisms involved in chemical and electrochemical reactions. For example, cyclic voltammetry technique was used to elucidate the origin of the electrochemical promotion in $Pt/Na_3Zr_2Si_2PO_{12}$ (NaSiCon) system [62]. Cyclic voltammogrames in Fig. 7 show typical cathodic and anodic peaks. The area of each peak corresponds to a quantity of charge passed between the working and counter electrodes. This electron transfer can be directly linked to the backspillover of sodium ions between the electrolyte and the catalyst.

5. Applications involving the deposition of (electro)catalyst thin films

There are many catalytic devices for which catalyst thin films with specific characteristics are an essential structural part of the system and a prerequisite of catalytic efficiency. Typical examples of devices are given hereafter for which catalyst thin films with well adapted structural and morphological characteristics represent an essential part. By way of illustration, different devices directed towards environment and energy technologies are described hereafter, involving electrocatalytic materials. Each of these examples shows that specific coating methods must be used in order to meet the requirements imposed by the design of the catalytic device. Typically electrocatalytic electrodes in fuel cells require macroporous layers allowing efficient fluid flow and can be advantageously prepared by using chemical methods. In this way, deposition of powder suspensions containing pore-formers, spray pyrolysis or electrophoretic deposition are able to produce several microns thick films with controlled porosity. When very thin mesoporous catalytic films are needed, like in microreactors, the sol–gel process will be preferred, especially for the preparation of ordered mesoporous structures with a high specific surface area. On the contrary physical vapour deposition methods are more suitable for the preparation of dense thin electrolytes or metal electrodes, for example in the case of gas sensors. More generally, new design of reactors aimed at the electropromotion of catalysis can take advantage of using together chemical and physical coating methods. It will allow the combination of high specific surface area catalyst supporting materials with conducting materials able to convey charged species involved in the electropromotion of catalytic reactions.

5.1. Fuel cell

A fuel cell is an energy conversion device that produces electricity and heat directly from a gaseous fuel by electrochemical combination of the fuel with an oxidant (Fig. 8). The SOFC cathode

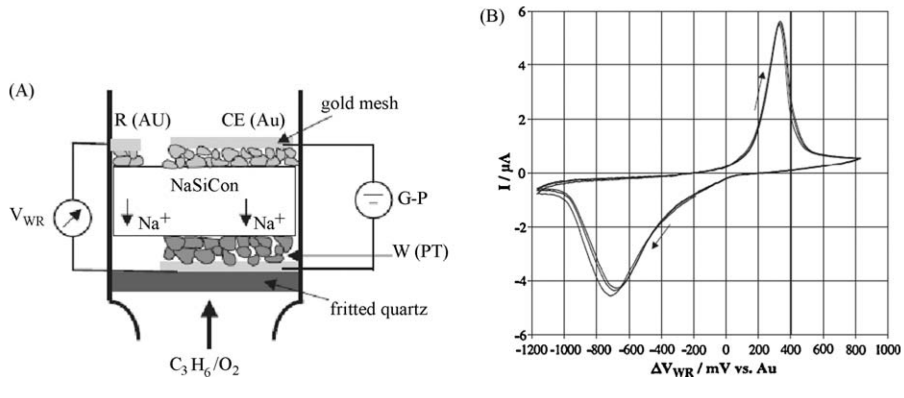

Fig. 7. (a) Schematic drawing of the electrochemical cell. (b) Cyclic voltamogrames at 200 °C under C_3H_6/O_2: 0.04%/8.3% atmosphere (scan rate: 10 mV/s) [62].

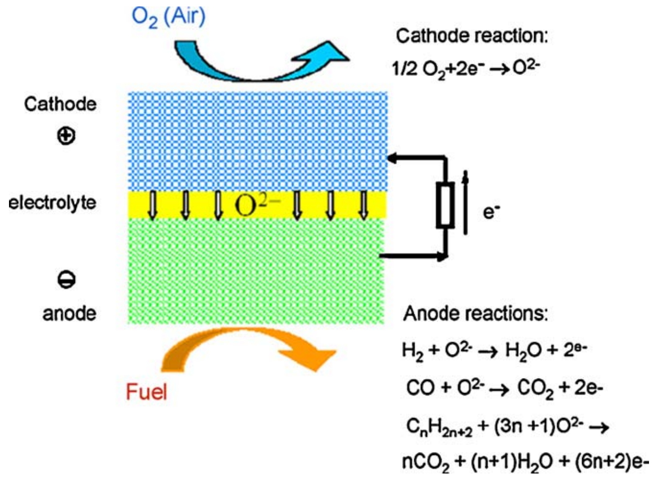

Fig. 8. Schematic representation of a solid oxide fuel cell and its working principle.

needs high electrocatalytic activity for oxygen reduction and the SOFC anode a high electrocatalytic activity in fuel conversion.

Decreasing operation temperature of SOFC down to 500–700 °C requires an increased ionic conductivity for the electrolyte (i.e. thin electrolyte and/or new electrolyte materials) and an enhanced electrode reaction activity. To do this many materials are investigated in the research world. To separate the influence of electrode morphology from intrinsic properties of the material, dense thin film microelectrodes are elaborated [63].

5.2. High temperature gas sensors

Gas-sensing devices can be used for different applications: continuous monitoring of the concentration of gases in the environment and premises, detection of toxic dangerous gases, drugs, smoke and fire, energy saving, anti-terrorist defense, health, amenity, control of automotive and industrial emissions, as well as various technological processes in industry [64]. For example, ceramic exhaust gas sensors are installed in quantities of millions in automotive exhaust gas systems. Almost any automobile being powered by a gasoline combustion engine is equipped with at least one zirconia exhaust gas oxygen sensor (λ) for detection of the air-to-fuel ratio. Besides this, another big environmental concern is the release of NO*x* into the atmosphere in the lean-burn condition of gasoline engines and now of diesel engines equipped with particle filters [65,66]. Therefore, for an accurate on-board diagnostic (OBD), direct measurement of the concentration of different gases such as CO, CH_4, NO, NO_2, CO_2 and other hydrocarbon gases is essential using low cost, fast response, high-selectivity solid-state gas sensors [67].

Typically a (high temperature) gas sensor can be considered as an electrochemical device based on an electrolyte supporting two thin electrodes and equipped with current collectors. Different sensing element geometries have been developed as shown in Fig. 9. Coating methods like sputtering, screen printing or sol–gel have been widely used for sensors development [66].

5.3. Microreactors

The aim of developing microreactors is primarily to minimize the complicated chemical plants due to their specific advantages. It has been shown that miniaturization can improve heat and mass transfer by decreasing the diffusion distance within the microreactor and increasing the interfacial area per unit reactor volume. Rapid mass and heat transfer rates were obtained even at laminar flow regime making microreactor an excellent choice for fast or highly exothermic reaction systems. Microreactors can suppress formation of hot spots and prevent runaway reaction enabling safe operation under otherwise dangerous conditions. Due to their small size, microreactors are also especially suited for endothermic reactions whose reactivity depends on the rate of heat input. That is one of their great strengths as a tool for process intensification, where the catalyst, products, or process may be sensitive to temperature. The precise spatial and temporal control over temperature, residence time, fluid flow and mixing is another advantage of microreactors.

For example the steam reforming of methanol is a highly endothermic reaction which can be carried out at medium and low temperatures so that it makes possible the direct utilization of reformate without subsequent processing to remove CO, in the case of a PEM anode electrocatalyst working at a temperature sufficient high to avoid poison effect of CO. The advantage of a microreactor wall-coated catalyst instead of using the catalyst in packed bed form has been shown for $CuO/ZnO/Al_2O_3$, a group of catalysts that shows a high steam-reforming activity for methanol at low temperature [68]. In this work quartz capillaries were chosen as microchannel reformer elements. A wash coating method similar to those used for catalyst deposition in honeycomb monoliths was applied to deposit the catalyst on the inner surface of the capillaries (Fig. 10). This wet chemical method has been preferred to other coating methods because it is well adapted to channel geometry but also due to the capacity to provide the high surface area required for catalyst reaction.

5.4. Environment remedial catalytic devices

The catalytic systems most widely used in environmental applications are based on monolithic reactors. Most of them exhibit a honeycomb structure which has been initially developed for exhaust gas treatment. They offer great advantages over pellet catalysts, in particular the low-pressure drop associated with the high flow rates that are common in environmental applications. Beyond automobile exhaust treatment, other environmental applications are now in progress like ozone abatement in aircraft; selective reduction of NO*x* in stationary systems; destruction of volatile organic compounds (VOC) from chemical plants, domestic sources and restaurants; catalytic combustion; and many other emerging applications. Monolith reactor designs different from

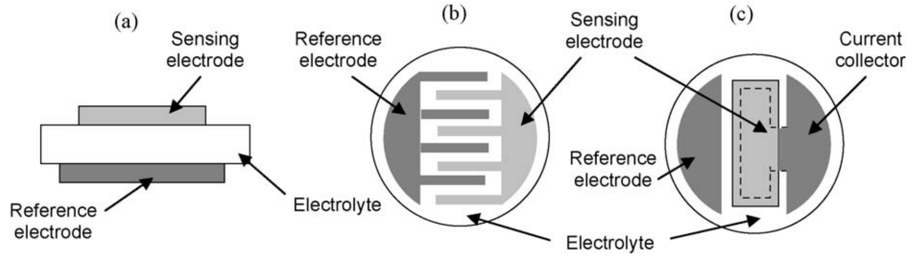

Fig. 9. Different sensor architectures based on electrolyte/electrodes arrangements. (a) Multilayer, (b) one face textured, and (c) interdigitated from [66].

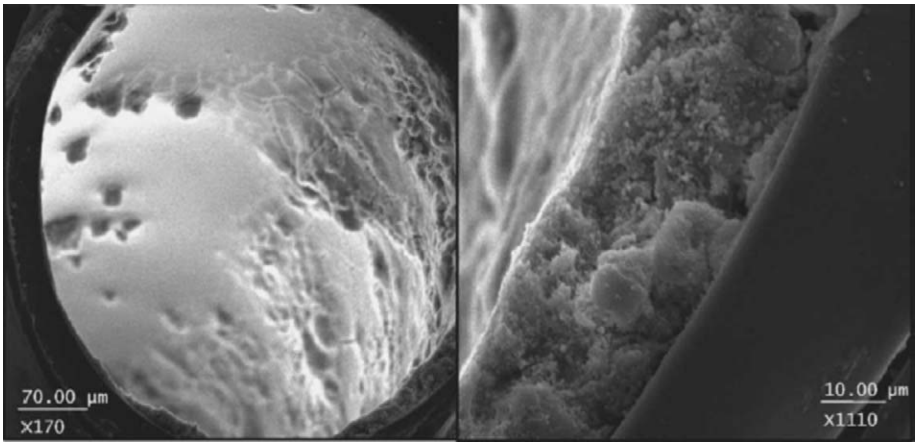

Fig. 10. Microchannel reformer based on quartz capillaries. Micronic $CuO/ZnO/Al_2O_3$ catalyst thin films on 530 μm fused silica capillaries, from [68].

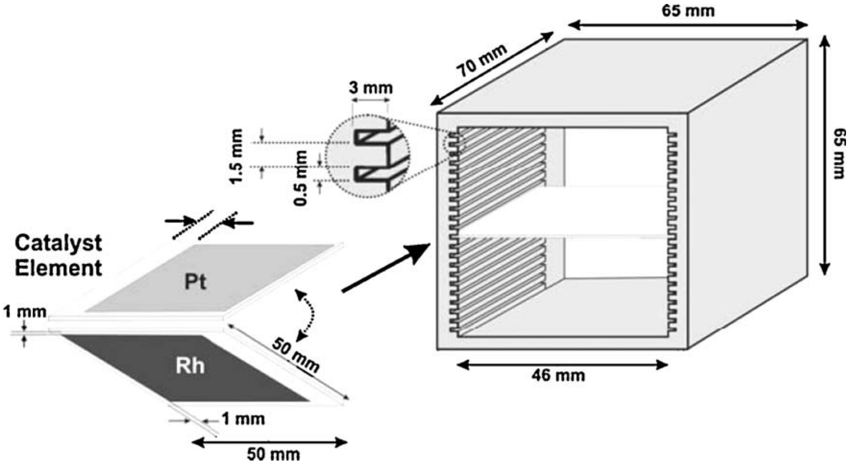

Fig. 11. Schematic of a monolithic electropromoted reactor (MEPR) from [70].

those based on honeycomb structures have been investigated. More detail on preparation technologies for monolithic reactors can be found in a recent review [69].

A specific design for a monolithic reactor in the field of electropromotion of catalysis (Fig. 11) has been recently reported [70]. Nitrous oxides have been recognized as harmful gas for environment. This monolithic-type electrochemical promoted reactor (MEPR) anticipates the effective control of nitrogen oxides (NO*x*) emitted from diesel and lean-burn engine. It is based on Rh and Pt sputter-deposited films on thin yttria-stabilized-zirconia (YSZ) plates and has been tested in simulated and real automotive exhaust gas.

5.5. Ceramic ion transport membranes for gas separation and catalytic reactors

Ion transport membranes (ITMs) are fabricated from ionic and mixed-conducting dense ceramic oxides that conduct oxygen ions and protons at elevated and medium temperatures. They are very selective to gas transport but they require deposition of thin electrocatalytic layers on both sides in order to convert in a reversible way, gaseous molecules into ionic species. Until now ITMs made of oxygen ion conducting materials are the most advanced for practical use. They have significant future potential for the industrial gas and energy industries with a wide variety of applications, for example the separation of oxygen from air, the conversion of natural gas to syngas or the production of hydrogen in steam electrolysis cells. The ITM materials and processes that are being developed can be categorized by focusing on the driving force that governs oxygen transfer across the membrane. As shown in Fig. 12a oxygen ion conductors with low electron conductivity can be used when a voltage is applied across them to separate and compress oxygen from a low-pressure source, for example air, to a high pressure product oxygen stream. Separators utilizing such membranes are designated as Oxygen Generators. In contrast mixed ionic and electronic conductors can be incorporated into processes which impose an oxygen partial pressure differential across the membrane at high temperature (Fig. 12b). This pressure gradient drives oxygen ions from the high partial pressure side to the low partial pressure side. Mixed-conducting ceramic membrane can be used also in processes for which a driving force for oxygen transport is developed by depleting the oxygen partial pressure on one side of the membrane through chemical reaction (Fig. 12c). This allows oxygen to be transported from a relatively low-pressure air feed to a higher pressure reaction product stream. This category of membranes has the potential for syngas production and is a key feature of the ITM Syngas process [71].

As for oxygen ion transport materials, high proton conducting solids can be used, in principle, as ceramic membranes equivalent to the aforementioned ITMs but for processing hydrogen and hydrogen-containing compounds [72]. These devices are based on an electrochemical cell in which the proton conducting solid is used as an electrolyte. They are investigated at a laboratory scale and still need the search for better proton conducting solids.

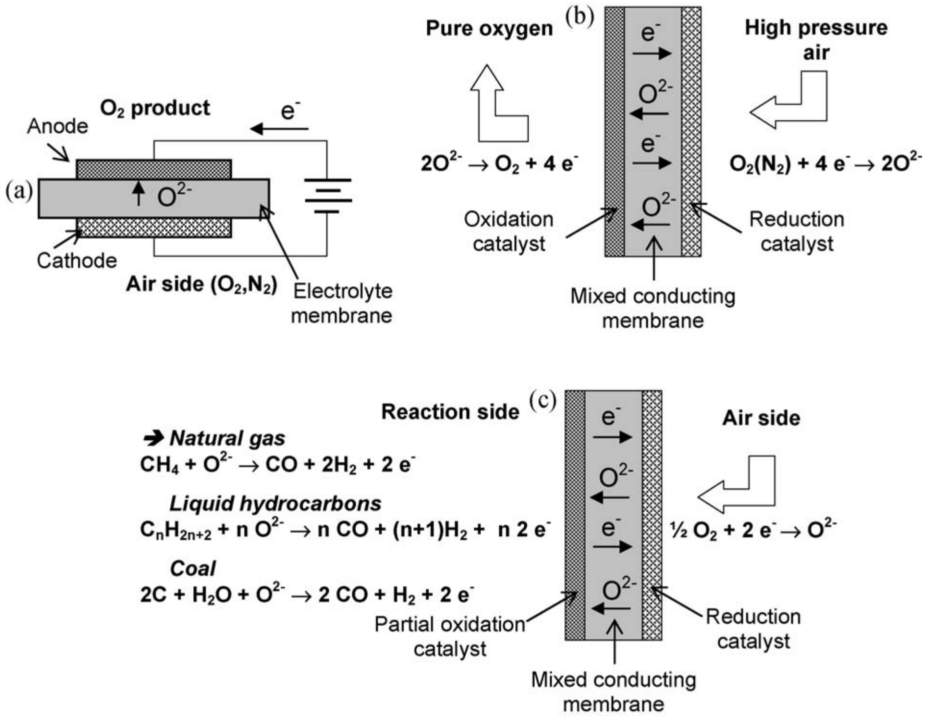

Fig. 12. Driving forces for oxygen ion transport membranes (ITMs) involved in gas separation and catalytic processes: (a) oxygen extraction using a DC power source (ionic conductor); (b) oxygen extraction using a pressure gradient (mixed ionic-electronic conductor); (c) oxygen extraction using a O^{2-} consuming reaction (mixed ionic-electronic conductor).

However they have potential interest as steam electrolyzers and steam pumps. The advantage of such electrolysis cells based on proton conductors is that pure hydrogen gas without water vapour can be obtained in contrast to those using oxide ion conductors [73].

6. Conclusion

This paper provides a short overview of open-issue challenges in the field of preparation and characterization of catalyst thin films. Special attention is paid to those involved in electrocatalytic devices based on conducting ceramic supports and more specifically on those of practical use for electropromotion of catalysis. The aim was to demonstrate that catalyst thin films play an important part in the design and the fabrication of catalytic systems involved in a number of emerging technologies. Most of these technologies address environmental problems or alternative energy production systems. The aforementioned examples of devices based on electrochemical principles, show that the control of shape, microstructure, porosity and composition of catalyst thin films is essential in order to make these devices catalytically effective and attractive commercially. Presently, a large number of preparation and characterization techniques have been investigated with the aim to prepare thin supported films for use in variety of technological area. Some of them can be advantageously used for the fabrication of catalytic systems requiring both electrochemical and catalytic properties. A judicious choice of these techniques can effectively help the development of EPOC systems in terms of materials cost minimization, ease of electrical connection and efficient reactor design.

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