

Advanced ceramic membrane design for gas separation and energy application

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9.1 Introduction

Ceramic membranes have been widely applied in the industrial and commercial sectors in addition to being an ongoing and expanding field among research communities. Recent progress in ceramic membranes includes the development of new functional materials, improvement of fabrication process, and control and tailoring of micro-structure. Ceramic membranes have gained significance in separation processes, particularly under harsh conditions, such as corrosive and high-temperature operations, owing to their high chemical, thermal, and mechanical stabilities (Li, 2007a,b; Tarpeh & Chen, 2021). It is noteworthy that dense ceramic membranes made from certain materials (e.g., perovskites and fluorites) can theoretically display infinite permselectivity for gases such as oxygen and hydrogen at elevated temperatures. Such ceramic membranes offer great potential for industrial gas separation with high requirements on purity. In addition, ceramic membranes with ionic conductivity serve as the core component for solid oxide fuel cells (SOFCs), also known as ceramic fuel cells, which are an important energy application. As the world's energy demand continues to grow, the development of more efficient and sustainable technologies for producing and storing energy is becoming more important.

Even though ceramic membranes can improve productivity for many reactions and separations in the chemical processes (Li, 2007a,b), they are more

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expensive than their polymeric counterparts. Current research progress has demonstrated that membrane-based technology has the potential to minimize cost, increase efficiency, and present environmentally friendly operation for energy production systems (Li et al., 2016a, 2020; Roy & Ragunath, 2018). These can be achieved through developing advanced micro-structured membranes for improved performances. This chapter focuses on the fabrication of advanced ceramic membranes for gas separation and energy applications with recent achievements at laboratory scale.

9.1.1 Micro-structured ceramic membranes

Ceramic membranes can be of various design types, such as flat sheet (planar), tubular, and the latest micro-tubular design after miniaturization. This chapter aims to highlight the micro-tubular structure, given the recent progress in the design process and applications. The first generation of ceramic hollow fiber membrane, developed via a ram extrusion process, is largely a single hollow channel design without any additional micro-structures. Such a membrane type is also called a micro-tube and lacks the surface area as a result of a low-porosity and symmetric design. Moreover, such micro-tubes face significant technical difficulties in reducing wall thickness, owing to the high pressure required to extrude a viscous paste. On the other hand, the recently developed phase inversion–assisted extrusion technique has demonstrated superior flexibility in micro-structure design and tailoring.

As shown in Fig. 9.1, the typical morphology of a ceramic hollow fiber derived from such a phase inversion process has two characteristic substructures: micro-channels (finger-like voids) and a sponge-like structure (Paiman et al., 2015; Wang & Lai, 2012). Image magnification of the cross-sectional area shows that there is a plurality of cylindrical-shaped and well-organized micro-channels sandwiched between a thick continuous structure on the shell side and a thin continuous barrier on the lumen side, which is called a sponge-like structure. Micro-channels are isolated pockets of space, while the sponge-like structure, which is more of a fine structure with less porosity, provides the robustness for the whole membrane. The integrity of such a unique structure is preserved following a high-temperature sintering process resulting in a well-interconnected ceramic bulk.

The continuously arranged ceramic particles create a barrier or separation layer at the shell and lumen sides. The thickness of these barrier layers can be adjusted, while the shape, size, length, and density of the micro-channels can be tailored during the fabrication stage. The plurality of micro-channels has been described to be effective in lowering resistance to gas transport, providing a membrane with greater permeation rates (Lu et al., 2018; Rabuni et al., 2018).

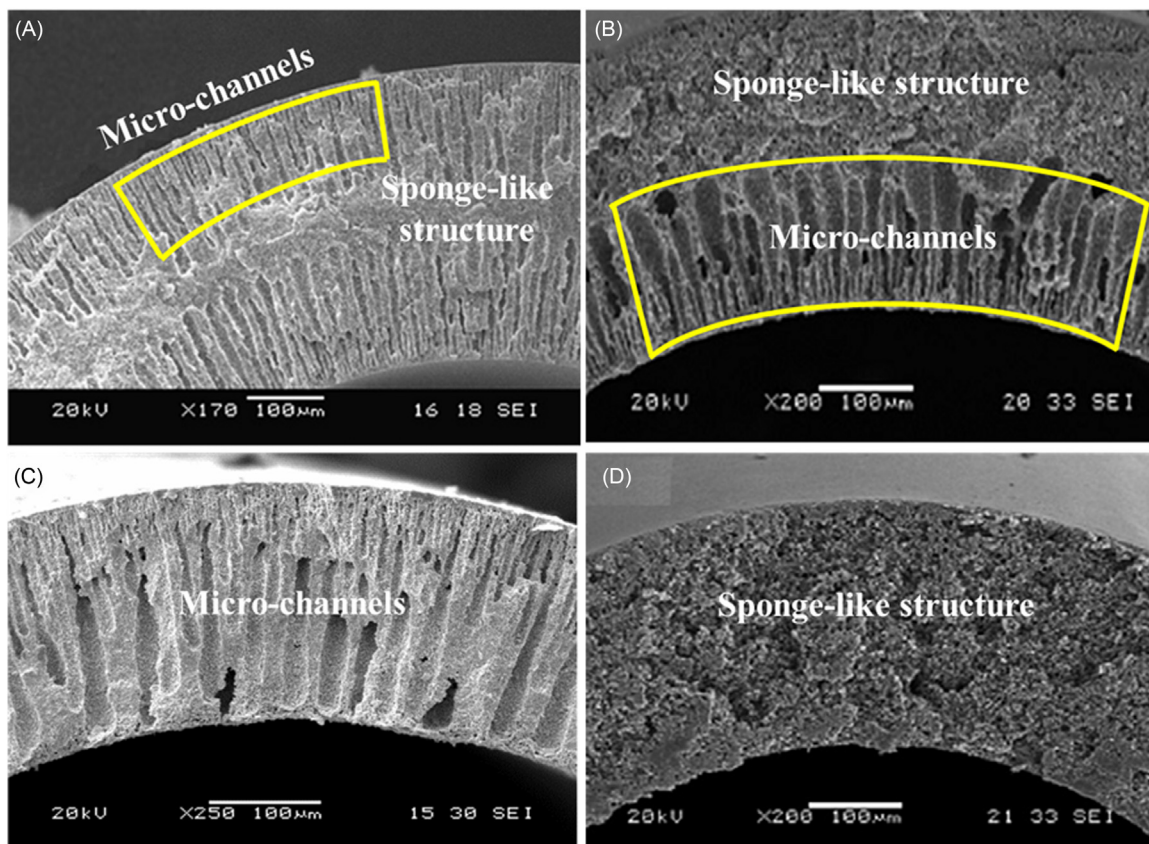


FIGURE 9.1

Examples of micro-structures of ceramic micro-tube. (A) Sandwich-like structure. (B) Typical micro-channel and sponge-like structure. (C) Open-channel structure. (D) Full sponge structure (Kingsbury & Li, 2009a).

Ceramic membranes have a critical limitation of intrinsic brittleness, particularly micro-tubes, owing to reduced dimensions. Such mechanical issues have often been overlooked or even compromised during attempts to improve membrane performance. It has also proven to be extremely challenging to achieve a balance between good performance and appropriate mechanical robustness without complicating the manufacturing by introducing an external support. Flexibility in micro-structure tailoring and morphology control through the phase inversion process could be exploited (Li, 2007a,b) to develop a better structural design for ceramic micro-tubes with better mechanical properties (Jamil et al., 2015). One option to improve the mechanical resistance of the micro-tube is the use of a multichannel design, analogous to a honeycomb structure (Lee et al., 2015b). Such a structure has

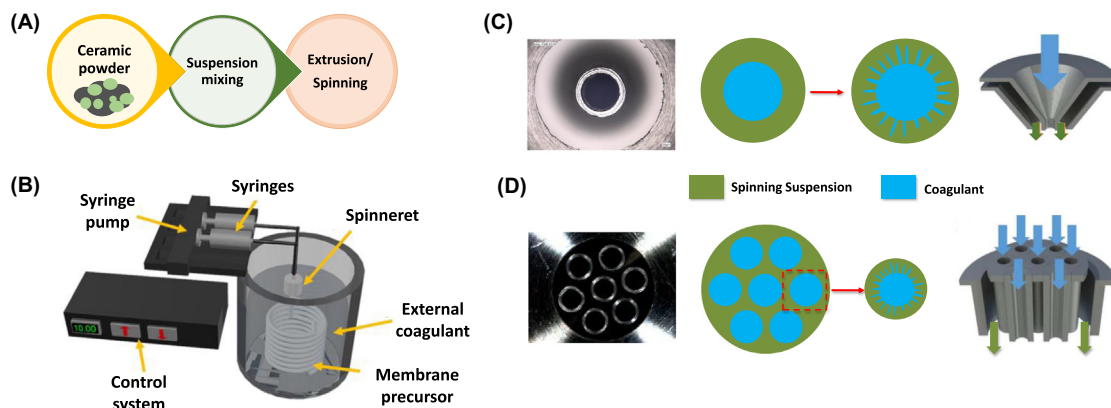
demonstrated superior robustness in comparison to the single-channel design. Using different types of ceramic materials, we investigated various multichannel capillary tubes via the phase inversion process in our previous work for different applications (Lee et al., 2015b; Li et al., 2019a,b, 2020).

9.1.2 Phase inversion—assisted fabrication

Phase inversion—assisted fabrication is analogous to ram extrusion but with an additional phase inversion step that occurs simultaneously during the extrusion process. The main distinctive feature is the spinning suspension, as the one for phase inversion—based extrusion has lower viscosity and much better fluidity in comparison to the plastic mass form for ram extrusion. During phase inversion extrusion the solidification of precursors occurs as a result of the solvent/nonsolvent exchange, whereas in the plastic ram extrusion process, the tubes are left to dry naturally right after extrusion (Jamil et al., 2015).

The fabrication of ceramic hollow fibers, or micro-tubes, via a phase inversion—based extrusion technique consists of three consecutive steps: (1) preparation of a spinning suspension, (2) extrusion of the precursors, and (3) the sintering process (Li, 2007a,b; Wu et al., 2013). The spinning suspension is prepared by mixing ceramic particles, solvent, binder, and additives. Ceramic as the main component must be selected cautiously, as the properties of the particle have substantial effects on the rheology and spinnability of the suspension and subsequently the characteristics of the final micro-tubes (i.e., pore size and porosity). The solubility and solvent power of the binder and the solvent influence the rate of phase inversion and solidification of the precursor and consequently the membrane morphology. In general, the solvents must have a high exchange rate with nonsolvents, as it will govern the structure of the produced micro-tube. Dispersants are added to the suspension for a better particle dispersion by disrupting the surface interaction between particles to ensure that they remain separated. To provide a high-volume fraction of ceramic particles in the spinning suspension, a minimum amount of additive must be added.

After the preparation of the spinning suspension, the next step is the extrusion process, also known as the spinning process. Before extrusion the spinning suspension must be degassed under vacuum and constant stirring to remove air bubbles, which may affect the micro-tubes' integrity and uniformity (Li, 2007a,b). After sufficient degassing time, the spinning suspension is extruded through the custom-designed spinneret, and concurrently, the internal coagulant (bore fluid) is pumped through the center bore of the spinneret. The extruded micro-tube goes into the nonsolvent coagulation

**FIGURE 9.2**

(A) General steps of a phase inversion—assisted extrusion process. (B) Schematic diagram of the extrusion setup, and in-house-made spinnerets. (C) Single-channel design. (D) Micro-monolithic (multichannel) design.

bath, where it forms a spiral, hence, the term “spinning.” During this process, the suspension inverts its phase from liquid to solid in the desired geometry.

Extruded micro-tube precursors are required to go through a heat treatment known as sintering. This process transforms a compact powder into a robust and denser ceramic body, during which the binders that are typically long-chain polymers soluble in the solvent must be fully removed. As the sintering process is carried out after the extrusion of the micro-tube, this method is known as the combined phase inversion—based extrusion and sintering technique. Fig. 9.2 shows the general steps of a phase inversion process, the experimental setup, and various in-house-designed spinnerets for achieving single-channel and multichannel designs.

9.1.3 Micro-channel formation and micro-structure tailoring

During the phase inversion process, the exchange between the solvent and the nonsolvent occurs, causing the polymer in the suspension to precipitate and consolidate the ceramic material. Typically, two morphologies have been observed: micro-channels (finger-like voids) and a sponge-like structure (Paiman et al., 2015; Wang and Lai, 2012), as shown in Fig. 9.1.

No agreement has yet been reached with regard to the mechanism that is responsible for the formation of micro-channels in ceramic membrane. One

explanation can be described by a hydrodynamically unstable viscous fingering. This phenomenon occurs at the interface between fluids with different viscosities in the first moments of mixing (Kingsbury & Li, 2009b; Paiman et al., 2015). There is a steep concentration gradient once the suspension is in contact with the nonsolvent, leading to a solvent/nonsolvent exchange. Subsequently, both a rapid increase in local viscosity and the precipitation of the polymer phase occur. However, owing to instabilities at the interface between the suspension and the precipitant, there is an inclination for viscous fingering to occur, initiating the formation of micro-channels. Under normal circumstances a stable interface would be established between the two phases of differing viscosities, but because of the presence of an invertible polymer binder, a rapid viscosity increase followed by polymer precipitation retains the viscous fingering structure (Kingsbury & Li, 2009b).

Lee et al. (2015a) has proposed to quantitatively interpret and mimic the formation of micro-channels using the Rayleigh-Taylor instability theory. Such a structure could be formed when two fluids with different densities are in contact. The low-density fluid (i.e., the external coagulant) inclines to push into the high-density fluid (i.e., the ceramic suspension) because of the interfacial instability and perturbation, during which solvent/nonsolvent exchange occurs. Further understanding of such process could help to better design and control the morphology as required by different applications.

It is generally accepted that the thickness of the sponge-like structure and the plurality of micro-channels have certain effects on the membrane properties such as the mechanical strength and permeation flux. Owing to the flexibility of the phase inversion process, controlling and tailoring the micro-tubes' morphology and structure are essential for developing membranes to suit particular needs (Kingsbury & Li, 2009b, Lee et al., 2015a, 2016). In essence, the phase inversion concept introduced in the 1960s was initially employed for making asymmetric polymeric membranes (Loeb & Sourirajan, 1963). A few decades later, our research group, led by Professor Li, started to apply this concept for making ceramic hollow fiber membranes, which are also known as ceramic micro-tubes (Li, 2007a,b). Since then, there has been significant progress whereby single-layer and multilayer ceramic micro-tubes have been successfully fabricated on the basis of single extrusion or coextrusion in producing micro-structured ceramic micro-tubes (Li et al., 2014d, 2015a; Othman, 2011; Othman et al., 2010, 2012). The most recent progress in fabricating multichannel ceramic membranes, known as micro-monolithic membranes, has enabled superior mechanical robustness in comparison to their single-channel counterparts, promising a long-awaited alternative to single-channel membranes that would allow the micro-tubular system to be commercially applied in the near future.

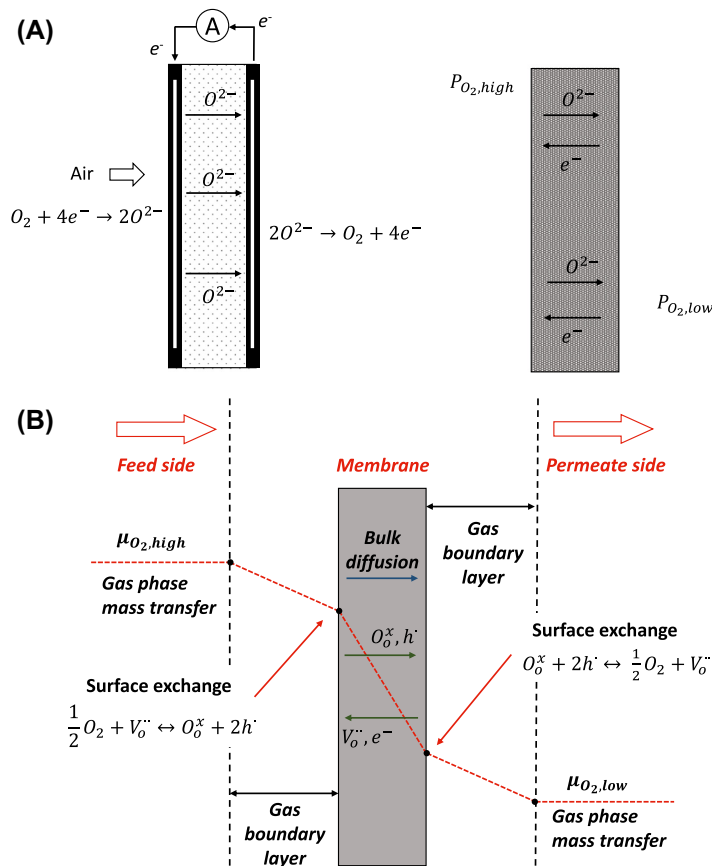
9.2 Oxygen-permeable membrane and membrane reactor

9.2.1 Oxygen transport in high-temperature ion conductors

Air separation is an important industrial process for pure oxygen or oxygen-enriched air production, which is extremely important in a wide range of applications, such as medical devices, rocket propellants, oxyfuel combustion, and chemical synthesis (Baker, 2002; Burdyny & Struchtrup, 2010; Hendriksen et al., 2000; Sunarso et al., 2008). Current technologies for air separation, such as cryogenic distillation and pressure swing adsorption (PSA), are well established and have been commercially applied for decades. However, these technologies are very complex, energy intensive, and costly. Therefore several noncryogenic approaches have been investigated in the past decades, among which a separation process using dense, ceramic oxygen-permeable membranes (OPMs) is a promising alternative. In principle, this chemical potential gradient-driven membrane process is energy efficient, despite requiring external heat to achieve the desired operating temperatures (typically above 800°C) to facilitate ionic conduction. In addition, one distinctive feature is that 100% oxygen permselectivity can theoretically be achieved, since a defect-free, dense ceramic OPM is solely permeable to oxygen and therefore no downstream posttreatment is needed (Allam, 2009; Sunarso et al., 2008).

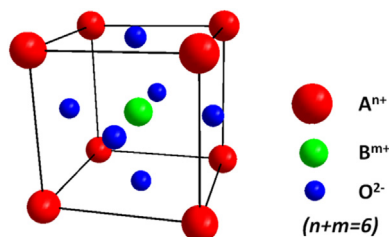
As for the materials of OPM, there are two major categories: pure ionic conductor and mixed ionic/electronic conductor (MIEC), the working principles of which are illustrated in Fig. 9.3A. Membranes made from pure ionic conductor require two additional electrodes (e.g., a precious metal electrode such as silver, gold, or platinum) to complete electron circulation and subsequently preserve electroneutrality. Despite the capability to precisely control the amount of produced oxygen, the additional requirement of electrodes and an external power source make this type of membrane less cost-effective and energy efficient for oxygen production. However, it finds a critical role in energy application as the electrolyte for SOFCs, which will be discussed in detail in Section 9.3. As for MIEC materials that exhibit mixed electronic and ionic conductivity, oxygen ions and electrons can be transported simultaneously to maintain electronic neutrality. Thus membranes made from MIEC materials can spontaneously transport oxygen ions at elevated temperatures and have attracted extensive research interest over the past few decades, which will be discussed in this section.

The development of new OPM materials has received significant attention to fulfill several general criteria, including high oxygen permeation flux, good chemical stability under different gaseous environments, proper mechanical strength, and cost-effectiveness, which have been covered in some comprehensive reviews (Chroneos et al., 2010; Hashim et al., 2010;

**FIGURE 9.3**

(A) Transportation of ions and electrons through (left) ionic conductor and (right) mixed ionic/electronic conductor. (B) Mechanism of oxygen separation via dense oxygen-permeable membranes.

Sunarso et al., 2017; Wei et al., 2013; Jie et al., 2020). Currently, perovskite-type oxides are among the most studied MIEC materials. The ideal perovskite structure with an ABO_3 stoichiometry is shown in Fig. 9.4, where A and B denote large and small cations, respectively, which have a total valence of +6. The larger A-site cations A^{n+} (e.g., La, Sr, Ca, and Pb) are of lower valence and have 12 coordinated, equidistant oxygen anions, whereas the small B-site cations B^{m+} (e.g., Ti, Ni, Fe, Zr, and Cr) have 6 oxygen anions coordinates. An ideal perovskite crystal structure is not capable of ion conduction. Therefore it is necessary for defects to be introduced within the lattice structure via approaches such as doping. The possible replacement of A^{n+} or B^{m+} with various lower valence cations could result in

**FIGURE 9.4**

Crystal structure of perovskites with ABO_3 stoichiometry.

a total charge $(n + m)$ less than 6. The net negative charge in the lattice is compensated by the formation of oxygen ion vacancies, denoted by $V_{\text{O}}^{\bullet}$ in Kroger-Vink notation and indicated by the $\text{ABO}_{3-\delta}$ oxygen nonstoichiometry in the general formula.

Fig. 9.3B illustrates the mechanism of oxygen separation. Given the assumption that the resistance from gas phase mass transfer is negligible, there are two major steps for the oxygen transporting process through the dense ceramic OPM, that is, surface exchange at both feed (oxygen-rich) and permeate (oxygen-lean) sides and bulk diffusion through the membrane. The molecular oxygen is first adsorbed onto the membrane surface with higher oxygen partial pressure and then dissociated into oxygen ions (O^{2-}). Driven by a gradient of oxygen chemical potential across the membrane, the oxygen ions are then transported to the oxygen-lean side, where they are converted back to molecular form before disassociating from the membrane surface. In the meantime, electrons flow in the opposite direction, forming a short-circuited electrochemical device without the need of an external circuit. It is widely accepted that oxygen permeation flux is jointly determined by both processes.

9.2.2 Design of high-performance oxygen permeation membrane

9.2.2.1 Micro-tubes with an open-channel micro-structure design

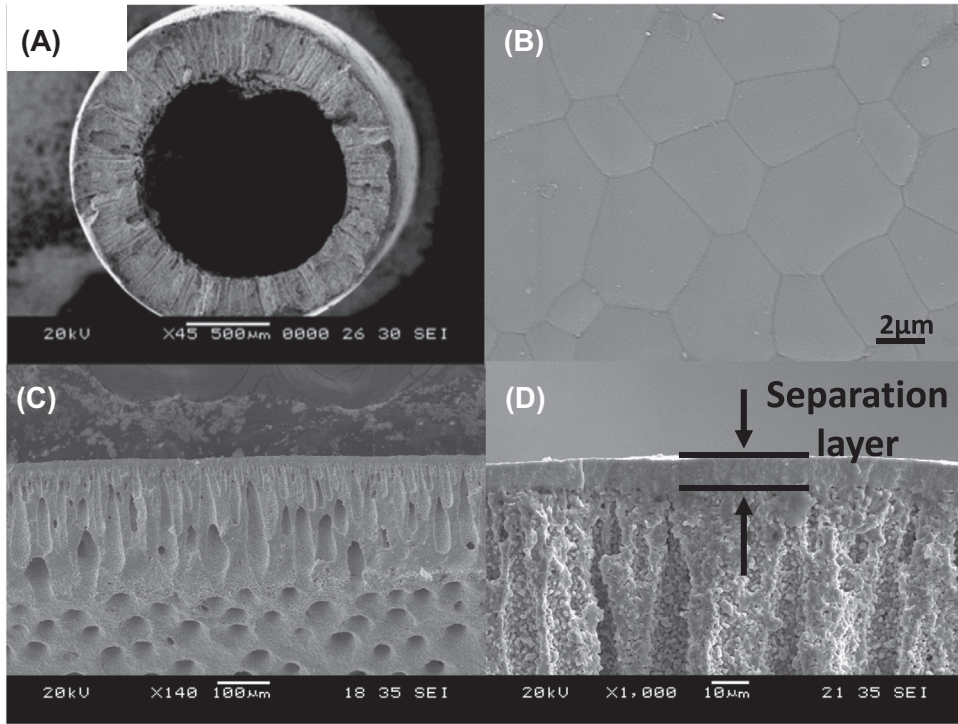
For decades, significant research has been conducted to investigate the potential of MIEC materials, particularly those with improved ionic conductivity. The design of OPM has received far less attention. Planar disk type is a geometry that has probably received the most interest, mainly because of the mature manufacturing process, such as tape casting. Air Products has constructed a demonstration module based on casted planar OPM, with a production rate of 5 tons per day (Carolan et al., 2009; Dyer et al., 2000). However, aside from relatively low separation area to volume ratios, the

sealing of such a system at elevated temperatures remains a major challenge that has yet to be solved. Additionally, the external mechanical support on which the thin OPM is typically deposited could show different thermal expansion behavior that leads to the accumulation of stress, consequently resulting in delamination and catastrophic structural failure. By contrast, tubular and the subsequently evolved micro-tubular (hollow fiber) design show the most important advantage of simplified sealing and high packing density. It is also suggested to be the optimal design based on the calculation of a full-scale module (Vente et al., 2006).

As was discussed earlier in the chapter, phase inversion–assisted extrusion exhibits the unique advantage of flexible micro-structure control and tailoring. Two typical morphologies are introduced during the process: micro-channels and sponge-like regions. For instance, when water is applied as the nonsolvent, the resultant morphology of micro-tubes normally includes two porous micro-channel regions sandwiched between two surface skin layers and a sponge-like region in the middle (Fig. 9.1A). If solvents are blended into the internal coagulant, such a morphology could be converted to the so-called open-channel micro-structure, which consists of only the outer skin layer and a plurality of micro-channels that penetrate the entire cross section, leaving circular entrances at the interior surface, as shown in Fig. 9.5. In this case, the outer skin with a thickness of less than 10 μm will function as the sole separation layer, showing a dramatic reduction in thickness from several hundred microns by more than one order of magnitude. From Liu et al.'s study (Liu et al., 2011), $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) perovskite micro-tubes that employed this “open-channel” micro-structure could provide up to 2.6 and 3.5 $\text{mL cm}^{-2} \text{ min}^{-1}$ of oxygen permeation flux at 950°C and 1000°C, respectively, with 75 mL min^{-1} of helium as the sweep gas, which is more than one order of magnitude higher than in the conventional design counterpart. However, such an effort to enhance oxygen permeation flux tends to compromise the mechanical robustness of the micro-tubes, whose brittleness is one major limitation for mass-scale applications. Therefore other approaches are urgently needed to achieve a better balance between oxygen permeation performance and mechanical strength.

9.2.2.2 Multichannel (micro-monolithic) design for highly robust oxygen permeation membrane

As was discussed in the previous section, by combining the advantages of thin separation layer thickness and high packing density, micro-tubular designs with micro-structure tailoring have exhibited significant potential. However, a long-existing trade-off between oxygen permeation flux and mechanical reliability is associated with conventional micro-tubes. The

**FIGURE 9.5**

SEM images of sintered $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ open-channel membranes. (A) Whole view of the cross section. (B) Outer surface of the membrane. (C) Cross section and interior surface. (D) Close-up view of the outer skin as the separation layer (Othman et al., 2015).

oxygen permeation flux could be calculated by using a simplified Wagner equation (Wagner 1975; Wei et al., 2013):

$$j_{\text{O}_2} = \frac{RT}{(4 \cdot F)^2} \sigma_{\text{amb}} \frac{1}{L} \ln \left(\frac{p'_{\text{O}_2}}{p''_{\text{O}_2}} \right) \quad (9.1)$$

In this equation, L denotes the separation layer thickness, p'_{O_2} and p''_{O_2} represent the oxygen partial pressure at the upstream and downstream sides, respectively, and σ_{amb} is the ambipolar conductivity, which is a material property and can be calculated on the basis of both ionic conductivity (σ_i) and electronic conductivity (σ_e), as $\sigma_{\text{amb}} = \frac{\sigma_i \cdot \sigma_e}{\sigma_i + \sigma_e}$.

According to Eq. (9.1), OPM should be as thin as possible to minimize diffusional resistance and subsequently maximize permeation flux. Different from planar OPMs, which typically include an external support, the separation layer in the self-supporting micro-tubular OPM also needs to function as the mechanical support. Therefore the reduction in thickness would inevitably

compromise the mechanical strength, which is a long-existing trade-off that has yet to be tackled. A new design featuring a good balance between high performance and good mechanical reliability is needed.

Lee et al. (2015b) reported a new miniaturized honeycomb-like design that exhibited superior mechanical strength and tube diameters well within the micro-tubular range. Such a design suggests a feasible solution to overcome the long-existing trade-off, as was proved in a subsequent work by Chi et al. (2017). By employing a custom-designed spinneret in which the single-nozzle configuration has been adjusted into a multinozzle design, the internal coagulant can be split into several streams before being in contact with the spinning suspension, thus resulting in the formation of multiple cylindrical lumens in parallel arrangement, as shown in Fig. 9.6.

The phase inversion–assisted extrusion technique has shown superior flexibility in dimension control as all three-, four-, and seven-channel designs display outer diameters ranging from 2.12 to 2.60 mm, which are well within the range of micro-tubular designs and result in decent theoretical outer surface-to-volume ratios of 1395–1711 m² m⁻³. While a comparable oxygen permeation flux up to 1.4 mL cm⁻² min⁻¹ was obtained in comparison to conventional micro-tubular counterparts, the maximum fracture load that

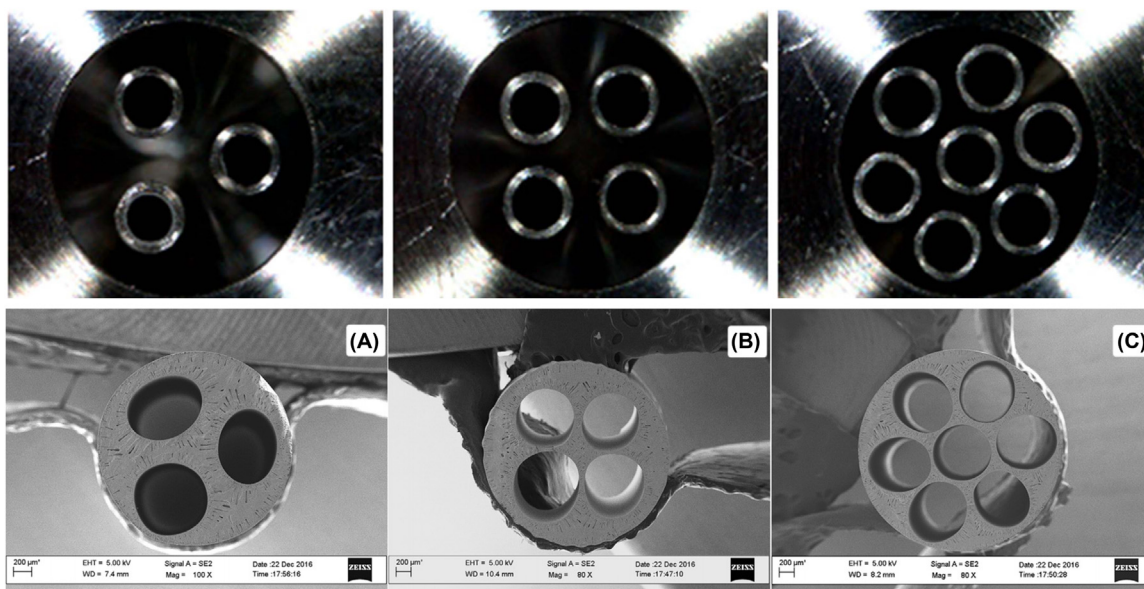


FIGURE 9.6

Configurations of (A) three-channel, (B) four-channel, and (C) seven-channel nozzle designs and cross-sectional SEM images of the sintered membranes (Chi et al., 2017).

the samples could withstand improved by up to 13 times, making the membrane samples much easier for bundling and scale-up. Moreover, there is room for further improvement, since this multichannel design has inherently provided a route to achieve both mechanical robustness and thin separation layer thickness.

9.2.2.3 *New bio-inspired design for next-generation oxygen separation*

As was mentioned earlier in the chapter, the recent multichannel (micro-monolithic) design involves the split of internal coagulant from a single stream to multiple streams, providing a new approach to enhance the mechanical strength of OPM while maintaining a relatively thin separation layer. The feasibility and effectiveness of such a design have been well proved in several earlier studies (Chi et al., 2017; Lee et al., 2015b).

In terms of the manufacturing of traditional micro-tubes, as shown in Fig. 9.7, the hydraulic pressure from the internal coagulant (or bore fluid) is critical in preserving a regular lumen geometry and preventing possible wrinkles or deformation, which is the usual case if the extrusion of coagulant is not sufficient. In the case of the six-channel design, as reported in Li et al.'s work, six nozzles were arranged in a hexagonal configuration, and multiple streams of internal coagulants were induced, as shown in Fig. 9.7F (Li et al., 2019a,b). Therefore the hydraulic pressure from the internal coagulant not only helps to prevent the buckling of the inner contour, but also enables further manipulation of such pressure to control and tailor the channel geometry. As depicted in Fig. 9.7, the hydraulic pressure of each individual stream can be offset in certain directions by the pressure from the neighboring internal coagulant. Given sufficient precipitation time, the lumen can expand in a nonuniform manner, and its geometry is transformed from circular to a droplet shape. It is also noteworthy that the use of a water-ethanol mixture as the internal coagulant instead of pure water is critical in this work to slow down the phase inversion process and provide sufficient time for channel deformation.

The resultant OPM has a morphology like the cross section of an orange, suggesting that the bio-inspired design includes the splitting the circular lumen into droplet-shaped sectors (sextants or octants). Most important, the arc of each sector has a degree of curvature that is close to the outer circumference, as shown in Fig. 9.7B. Compared to the multichannel design that was reported in previous studies, a maximum oxygen permeation flux up to $1.87 \text{ mL min}^{-1} \text{ cm}^{-2}$ at 950°C has been reported, which is more than threefold higher in comparison with the unoptimized counterpart and compares well with the open-channel design discussed earlier in the chapter. Such bio-inspired design has maintained the mechanical characteristics as reported before, showing a maximum fracture load of approximately 9 N, which is more than one order of magnitude higher than that of the open-channel counterpart.

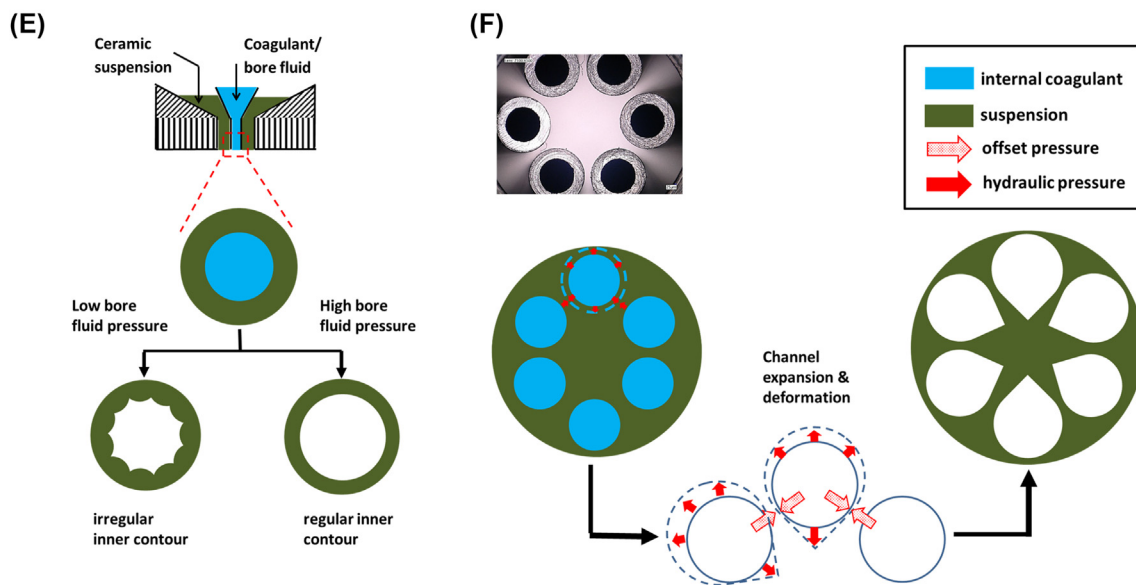
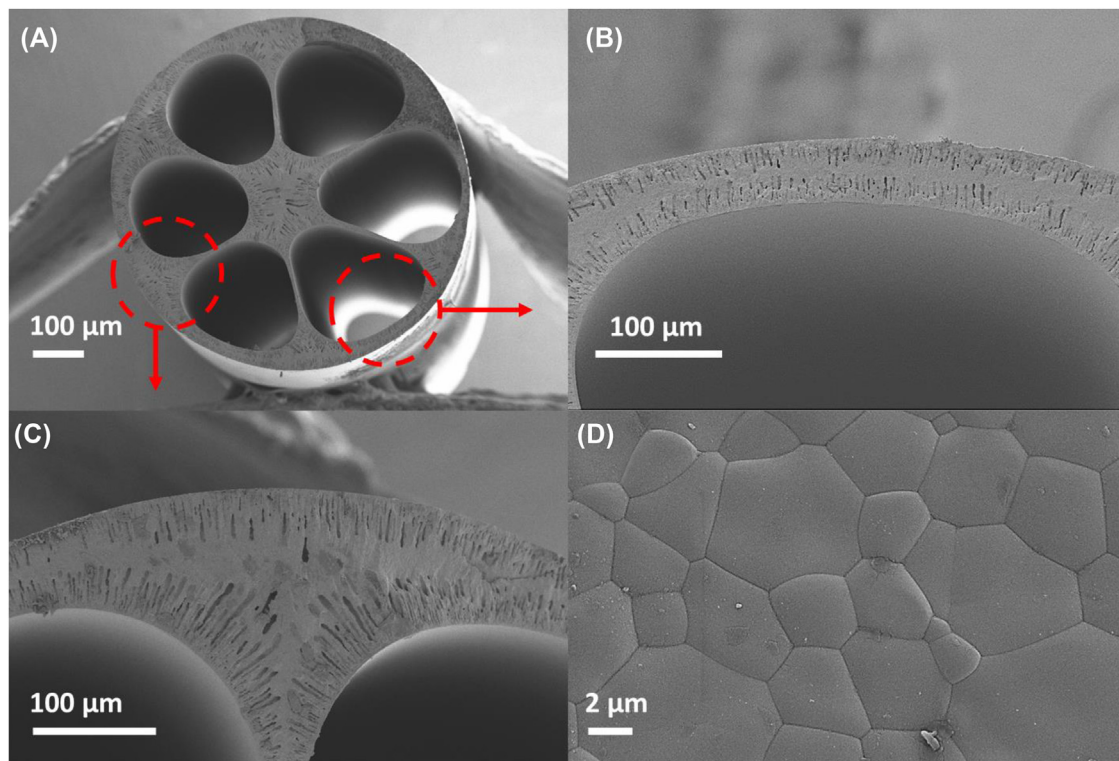


FIGURE 9.7

SEM images of sintered $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-8}$ membranes with a bio-inspired design. (A) Whole view. (B) Separation layer with a relatively uniform thickness. (C) Cross section of the wall between the shell and two bores. (D) Outer surface of membranes. Schematic diagram of (E) normal and irregular inner contour in a conventional hollow fiber membrane and (F) a bio-inspired six-channel micro-monolithic membrane geometry control (Li et al., 2019a,b).

9.2.3 Catalytic reactor based on oxygen-permeable membrane

To better exploit the potential of micro-structured OPM, Othman et al. carried out a series of studies by constructing a OPM-based microreactor for reactions such as partial oxidation of methane (Othman et al., 2013) and more valuable oxidative coupling of methane (OCM) (Othman et al., 2014). OCM is a chemical process that directly converts methane into the C_{2+} products (e.g., ethylene and ethane), which are of more industrial value. However, despite enormous research interest in the development of suitable catalysts, it is generally accepted that the major bottleneck that prohibits the commercialization of the OCM process is the trade-off between methane conversion and C_{2+} selectivity, which is mainly due to the presence of various side reactions.

Previous research has showed that a membrane reactor could potentially offer a higher C_{2+} selectivity over a conventional fixed-bed reactor or fluidized-bed reactor, particularly when an OPM functions to supply and distribute the oxygen, maintaining a local methane-to-oxygen ratio that is preferable for OCM reaction. The overall process is expressed as follows:

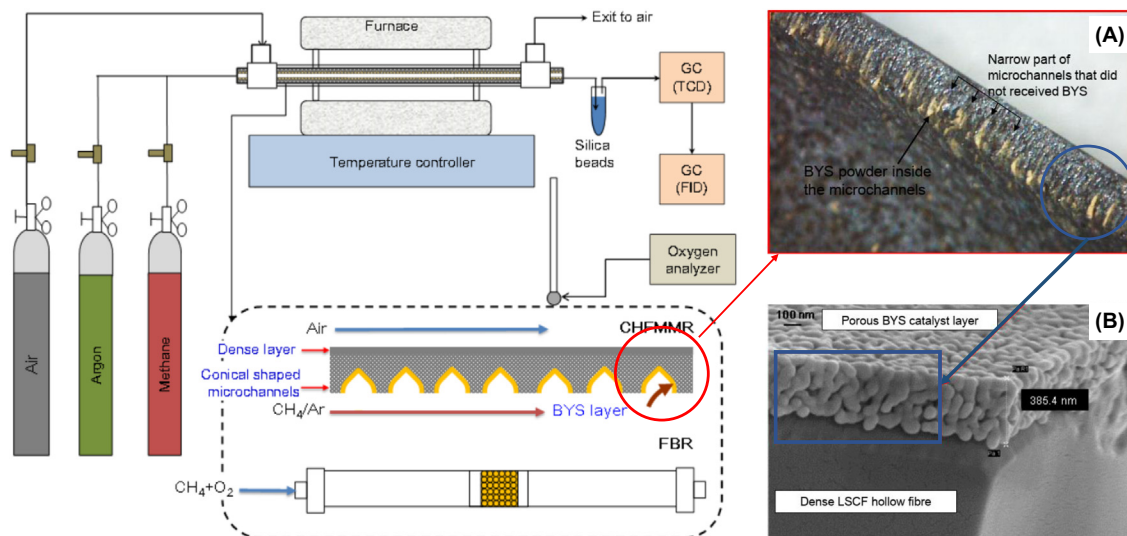


The overall equation is



As was mentioned earlier in the chapter, OPM is solely permeable to oxygen, which allows air to be used directly as the oxygen source without the complex separation process, resulting in improved cost-effectiveness. In addition, there is no direct contact between oxygen and methane in gaseous forms, prohibiting deep oxidation that produces CO_2 .

In the most recent study conducted by Othman et al. (2015), $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) catalyst was incorporated into the micro-channels of LSCF oxygen permeation membrane via an in situ sol-gel technique, leading to a thin layer (300–500 nm) of nano-sized BYS particles uniformly deposited along the inner surface of the whole membrane reactor, as shown in Fig. 9.8B. In comparison to conventional fixed-bed reactor, OPM-based microreactor has been proved very effective to overcome the long-existing trade-off between methane conversion and C_{2+} yield, showing a maximum value of 79% and 39%, respectively, which

**FIGURE 9.8**

Schematic diagram of an oxidative coupling of methane experimental setup for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ membrane with in situ prepared $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta}$ (BYS) catalyst. Microscopic images of (A) BYS powder deposited in micro-channels and (B) high-resolution images showing the thickness of the nanolayer BYS coating (Othman et al., 2015).

is the best performances reported so far. In addition, the uniform distribution of nano-sized BYS catalyst inside micro-channels has significantly facilitated the gaseous reactant to access the active sites, leading to a fourfold increment in C_{2+} productivity in comparison to the wash-coated membrane reactor counterpart (Othman et al., 2015).

9.3 Ceramic membrane in energy applications

Exploiting alternative energy sources has been a growing concern because global fossil fuel reserves are limited and constantly being depleted. While the emergence of green energy sources, such as wind, solar, geothermal, and hydroelectric energy, could reduce dependence on fossil fuels, there are major drawbacks related to financial and technical challenges. For the past decades, interest in utilizing ceramic membrane for energy applications has been growing rapidly. As was discussed earlier in the chapter, dense ceramic membranes with pure ionic conductivity function as the electrolyte, which is the core component that not only conducts the oxygen ions between electrodes, but also works as the physical barrier to prevent direct contact between

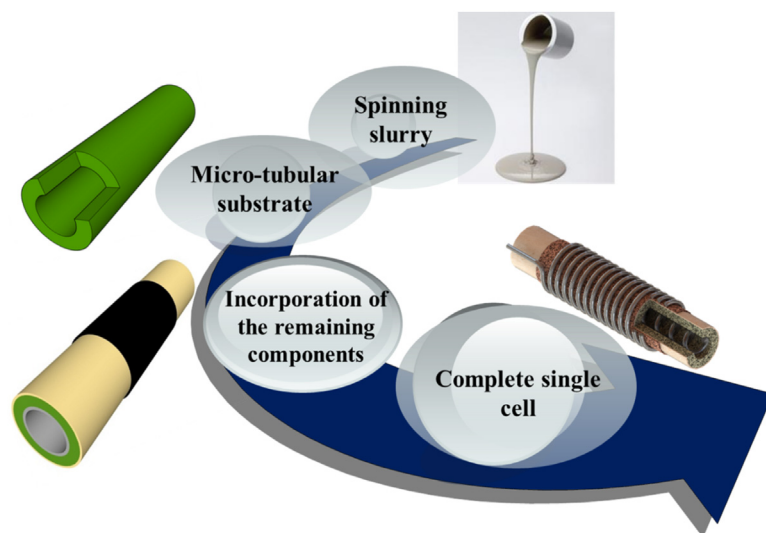
gaseous fuels and oxidants. The emergence of ceramic made from various materials with unique micro-structured designs has demonstrated promising outcomes. Micro-tubular membranes made via phase a inversion–assisted process have seen continuous improvement in further optimizing the appropriate design for desired applications.

9.3.1 Solid oxide fuel cell

The high operating temperatures for SOFCs, ranging from 6000°C to 1000°C, have enabled flexibility in fuel intake (Abdalla et al., 2018; Mekhilef et al., 2012), allowing various fuels aside from H₂ to be applied, including biogas, landfill gas, and fossil fuels. This is due to the internal reforming facilitated at elevated temperatures, which means that hydrocarbons and reforming agents can be fed directly into the anode compartment without the need of an external reformer. This high operating temperature also activates electrochemical oxidation of hydrocarbon fuels in the presence of catalysts. Additionally, the heat that is produced could be utilized via integrating a downstream process to achieve even higher overall system efficiencies. For example, the surplus heat can be used in an integrated gas turbine system, allowing a coproduction of heat and power, a process known as combined heat and power (Elmer et al., 2015). This heat recovery system, together with the energy generation, contributes to an overall system efficiency up to 60%–85% (Ellamla et al., 2015; Stambouli & Traversa, 2002; Wilberforce et al., 2016).

Geometrically, planar and tubular are the two common designs of SOFC. More recent micro-tubular designs (MT-SOFC) with a reduced geometric scale present additional technological advantages. These include better resistance to thermal shock, higher volumetric power density compared to larger tubular design, and quick startup and shutdown (Howe et al., 2011; Lawlor, 2013). Fig. 9.9 shows the steps that are involved in the fabrication of a complete single cell of a micro-tubular design.

Hydrogen (H₂) is a standard fuel for fuel cell operation. However, there are several challenges related to its use as fuel. One is that H₂ generation consumes a considerable amount of energy. At present, the primary sources for producing H₂ are 48% from natural gas, 30% from the refinery, and 18% from coal (Armor, 1999). About 20%–30% of the fuel value of hydrocarbons is lost during hydrogen production (McIntosh & Gorte, 2004). Hydrogen is also well known to be difficult to handle and store. Other major concerns include the costs of plant construction and development of the infrastructure. It is predicted that the financial requirements for worldwide pipeline-based distribution stations could reach \$20 trillion by 2030 (Ge et al., 2012).

**FIGURE 9.9**

Typical steps involve during the fabrication of a complete single cell (Cooper, 2016).

In standard SOFCs, since O^{2-} ions are the species that travel through the electrolyte, any combustible fuel can theoretically be utilized. Because the numerous hurdles associated with H_2 have yet to be solved, the SOFC running on hydrocarbons is desirable. A number of studies with SOFCs fueled by hydrocarbons have been reported in the literature, signifying the prospect of using substances other than H_2 as a fuel for SOFC (Gorte & McIntosh, 2004; Gorte et al., 2000, 2002, 2004; Li et al., 2020; Rabuni et al., 2018). There has been considerable interest in developing a protonic conductive electrolyte as an alternative to the O^{2-} ion-conducting electrolyte (Cowin et al., 2011; Fabbri et al., 2010; Ge et al., 2012; Mahato et al., 2015). Materials such as yttrium-doped barium zirconate and yttrium-doped barium cerate can be applied as an electrolyte (Fabbri et al., 2008; Li, 2015). These proton-conducting oxides have been reported to offer improved conductivities and to be almost as efficient as the state-of-the-art oxide-conducting ceramic (Duan et al., 2015). Their feasibility for conducting protons at low operating temperatures opens up the attractive prospect for SOFC operation at much lower temperatures compared to the present temperature range (Duan et al., 2018). However, some major drawbacks include the cost issues associated with proton-conducting materials and challenges during the sintering process [6]. Overall, the selection of the most appropriate electrolyte material for a particular application is crucial to ensure long-term stability and cost-effectiveness.

9.3.2 Coextrusion of functional membrane for high-performance micro-tubular-solid oxide fuel cells

In earlier studies conducted by Othman et al., a coextrusion and cosintering technique has been shown to be very effective in simplifying the fabrication procedure and enhancing the interlayer adhesion (Othman et al., 2010, 2011, 2012). Decent performances have been reported for MT-SOFCs in which an anode/electrolyte dual-layer membrane was involved. In addition, dual-layer and later triple-layer coextrusion have enabled more complicated designs for SOFC with various functional layers induced to achieve improved performances (Li et al., 2014b,d, 2015a,b). It is noteworthy that for conventional layer-by-layer fabrication, the incorporation of such functional layers is very tedious and time and energy intensive.

Li et al. carried out a series of studies to exploit the potential of triple-layer coextrusion by investigating two designs: anode–anode functional layer (AFL)–electrolyte and current collector–anode–electrolyte, as illustrated in Fig. 9.10 (Li et al., 2015a,b).

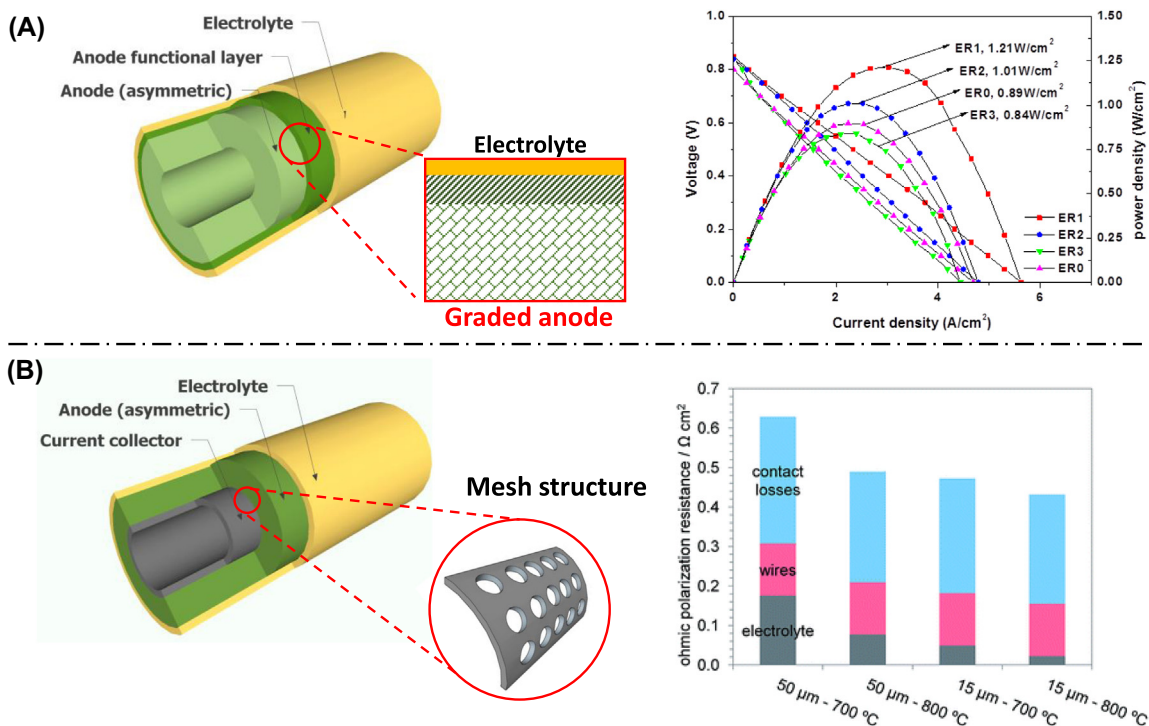


FIGURE 9.10

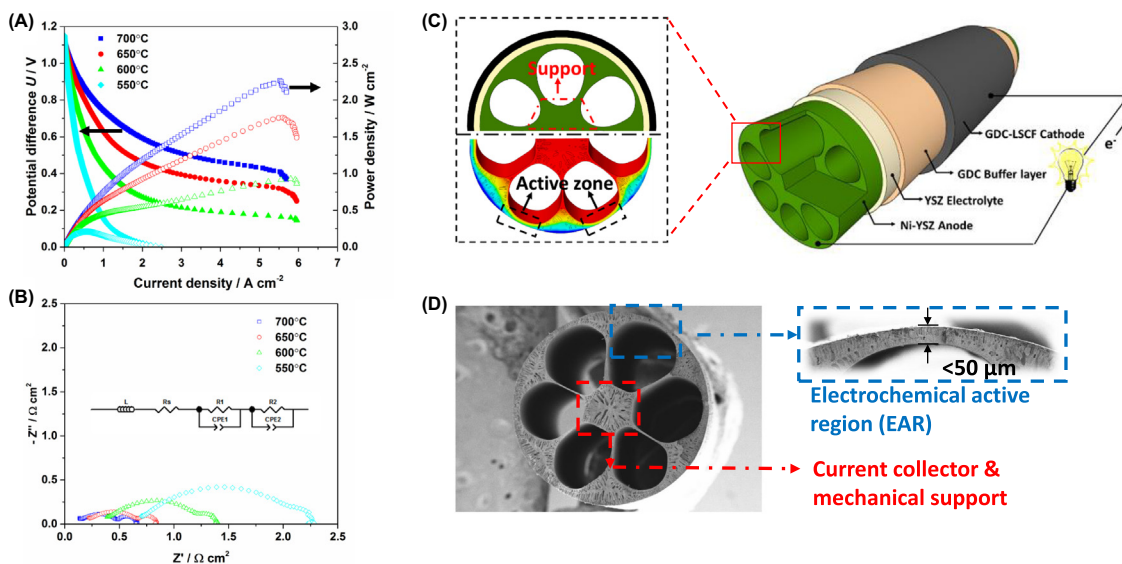
Triple-layer designs of (A) anode- anode functional layer -electrolyte and (B) current collector-anode-electrolyte.

In the first work of triple-layer design with an anode functional layer (Li et al., 2015a), a graded anode structure was developed in a single-step process, as shown in Fig. 9.10A. During the development of a micro-tubular SOFC, the design is of equal importance as new materials for cell components. To achieve both improved gas transport and an enlarged triple-phase boundary inside the anode, the concept of an AFL was first proposed by Virkar et al. (2000) during his attempts to decrease the activation and concentration polarizations by employing a graded anode. By adjusting the composition of the slurries, the support layer is coarser with a bigger grain size and higher porosity to facilitate the gas transport of both fuels and reaction products (e.g., steam and CO_2), which helps to reduce the concentration polarization. Moreover, a finer structure has been introduced right next to the electrolyte for more reactive sites, so the activation polarization may well be inhibited. It has been reported that the additional AFL, whose thickness can be well controlled between 16.9 and 52.7 μm , not only enhanced the mechanical strength by up to 84%, but also improved the electrochemical performances by 30%, showing a maximum power density of 1.21 W cm^{-2} at 600°C , which is one of the best performances reported for intermediate-temperature operation (Li et al., 2014c, 2015a).

As for the other triple-layer design (Li et al., 2015b), a nickel-based current collector was incorporated simultaneously via coextrusion, as shown in Fig. 9.10B. If MT-SOFCs are to be applied for large-scale application, a critical challenge is effective current collection, especially from the lumen side of individual cells with very limited dimensions. The common technique that has been developed for lumen-side current collection involves the use of a combination of both precious metal wires and paste, including silver, platinum, or gold. Such a technique is quite complicated, costly, and labor intensive; therefore it is not suitable for mass-scale production. Reproducibility and contact loss are other concerns in evaluating the overall cell performance. Some previous numerical calculations have suggested that the contact loss resulting from problematic adhesion between the anode and metallic wires could be the major contributor to ohmic loss (up to 70%) (Droushiotis et al., 2013). On the other hand, the nickel-based current collector layer was fabricated simultaneously with the anode, which not only leads to significantly improved adhesion, but also reduces the cost to eliminate the need for previous metals. The cell displayed a decent performance of 1.07 W cm^{-2} at 600°C , while the ratio of contact loss to total ohmic loss was dramatically reduced from more than 70% to 6%–10% (Li et al., 2014a, 2015b).

9.3.3 New micro-monolithic solid oxide fuel cell and utilization of waste methane

As was discussed earlier in the chapter, the multichannel (micro-monolithic) design has demonstrated superior mechanical robustness, which is one of the

**FIGURE 9.11**

(A, B) Electrochemical performances of a micro-monolithic ceramic fuel cell. (C, D) Schematic diagram of the active region and support separation (Li et al., 2020).

key requirements for the construction of a scalable MT-SOFC. Li et al. have developed the so-called micro-monolithic ceramic fuel cells by incorporating the design into anode substrate, as shown in Fig. 9.11 (Li et al., 2020). One major characteristics of such design is the highly asymmetric structure and the deliberate separation of mechanical support from the electrochemical active region, which markedly facilitates the mass transport of gaseous fuels. The diffusional pathway length for the fuel to reach active sites has been reduced from several hundred microns in conventional designs down to less than $50 \mu m$, shortened by more than one order of magnitude. The improvement leads to minimized concentration polarization and better performances, as shown in Fig. 9.11A and B. A maximum power density of $2.3 W cm^{-2}$ at $700^\circ C$ has been reported from using hydrogen fuel, which is superior to the best-performance planar counterparts (Shimada et al., 2016). In addition, the micro-monolithic design demonstrated excellent mechanical robustness and can withstand an external fracture load which is up to eight times higher than that of the micro-tubular SOFCs. Therefore such a holistic design has integrated advantages from various conventional designs and shows great promise for mass-scale applications.

To further exploit the potential of micro-monolithic design, Li et al. extended the application of hydrocarbon fuels, featuring low calorific value gas (LCVG) (Li et al., 2020). Despite the importance of methane in the global

energy blueprint, many methane sources remain untapped globally, owing to the low concentration and consequently low heating value. The methane in LCVG will not be useful until the concentration can be increased to pipeline natural gas grade, which requires a significant investment. In addition to such economic concerns, LCVGs impose tremendous threat to the global climate, since methane has a global warming potential that is 25–34 times higher than that of CO₂. Owing to the high working temperature, ceramic fuel cells become a promising candidate to utilize LCVGs directly via the internal dry reforming of methane reaction:



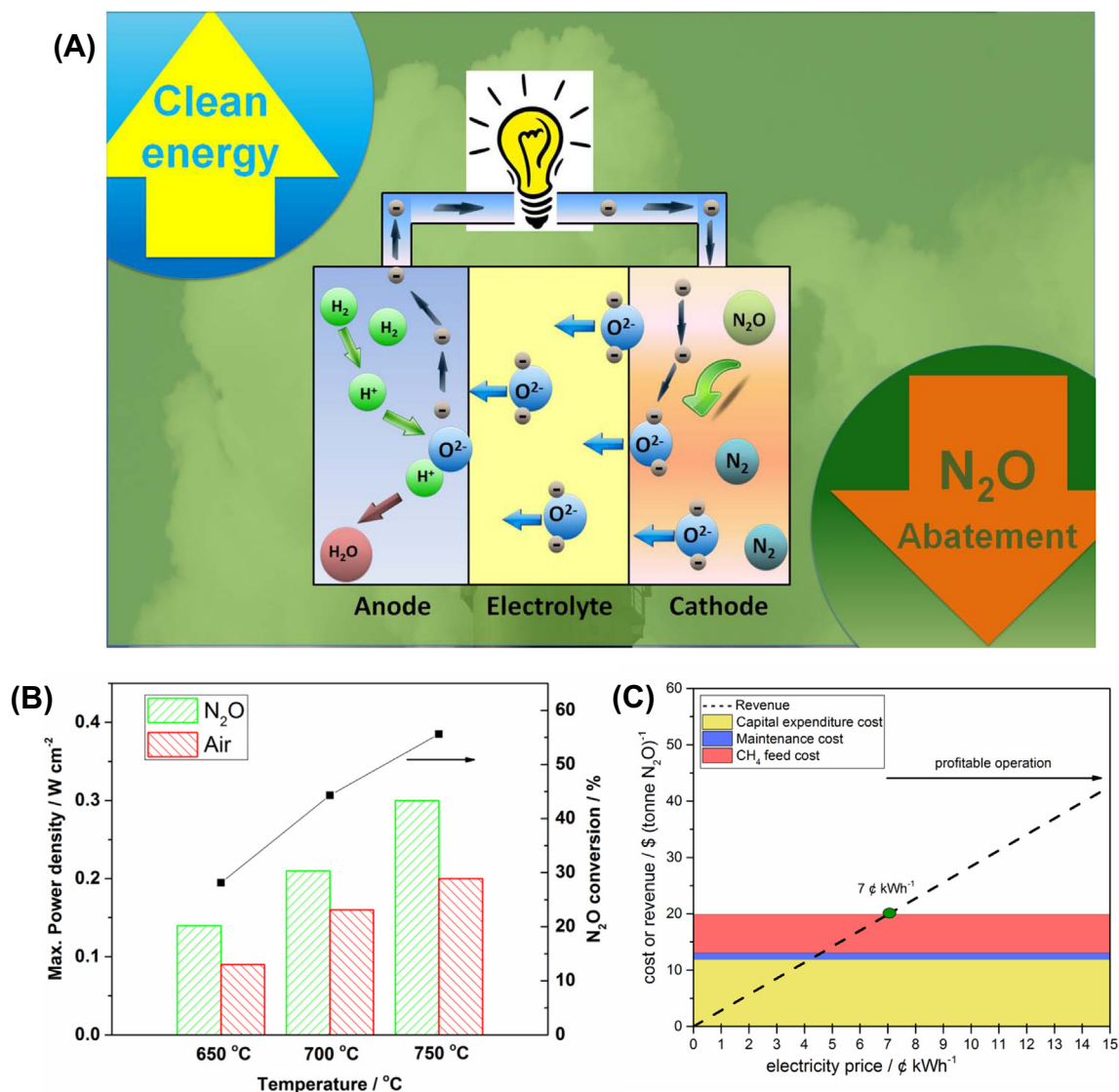
Owing to the optimization in gas transport, the micro-monolithic ceramic fuel cells showed excellent performance despite low methane concentrations, showing maximum power densities of 1.77 and 2.22 W cm⁻² at 700°C with 10% and 20% methane concentration, respectively. These performances are more than one order of magnitude higher than that of the planar counterpart fed by fuels with the same composition (Lyu et al., 2018).

9.3.3.1 Greenhouse gas abatement using ceramic fuel cells

Based on the micro-monolithic design, Li et al. further extended the application from energy generation to greenhouse gas abatement, featuring the abatement of nitrous oxide (N₂O), which is also known as laughing gas (Li et al., 2016a). In terms of global climate change, N₂O has an atmospheric heat-trapping ability that is 300 times stronger than that of CO₂, making it one of the six major greenhouse gases, according to the Kyoto Protocol. As for the major sources of N₂O emission, effluents from industries manufacturing adipic acid or nitric acid contain a high percentage of nitrous oxide, up to 60%, with catalytic decomposition using expensive precious metal being the main approach (Bernauer et al., 2020; Konsolakis, 2015). Li et al. (2016b) introduced N₂O into the cathode instead of air, and it functioned as the oxidant with the presence of LSM cathode as the catalyst. The results showed that as a result of improved oxygen partial pressure at the cathode side, N₂O could provide even better power output in comparison to air, with almost 60% of the decomposition rate. More interestingly, the electricity that is generated could offset the abatement cost of N₂O, showing the potential cost-free abatement of this greenhouse gas, as shown in Fig. 9.12.

9.3.3.2 Three-dimensional characterization of ceramic membrane

In investigating the morphological features of ceramic membranes, conventional characterization tools, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM), are all two-dimensional (2D) imaging techniques, providing limited insight into the three-dimensional (3D) spatial distribution of the micro-structure. In addition, a good number

**FIGURE 9.12**

(A) Concept of simultaneous greenhouse gas abatement and clean energy generation using ceramic fuel cells. (B) Electrochemical performance comparison between air and nitrous oxide as oxidant. (C) Technoeconomic analysis of greenhouse gas abatement using ceramic fuel cells (Li et al., 2016b).

of repetitions are necessary to obtain statistically relevant results. During the past decade, focused ion beam SEM has received significant research interest (Dai et al., 2015; Karen Chen-Wiegart et al., 2012; Kennouche et al., 2016; Vigié et al., 2013), as it enables the understanding of the micro-structure

variation in three dimensions under the surface. However, the long data acquisition time imposes strict limitations on the sample volume to be investigated. Moreover, this destructive approach makes repetition impossible. X-ray computed tomography (X-CT) has been used almost exclusively for medical diagnosis because of its nondestructive nature, which is one of the essential requirements for in situ 3D visualization and characterization of materials. While the sample is illuminated by an X-ray beam, sequential 2D projections of the sample can be obtained at regular increments, and these are subsequently back-projected to form a virtual 3D volume. [Lu et al. \(2018\)](#) and [Li et al. \(2020\)](#) have carried out extensive studies on 3D characterization of ceramic membranes with sophisticated morphology using the latest micro-CT and nano-CT, as shown in [Fig. 9.13](#).

In terms of ceramic membranes with complicated morphology, such as the highly asymmetric micro-monolithic design, micro-CT could provide a virtual 3D reconstruction with all morphological features included. In addition, such features, including micro-channels and sponge-like porous structure, could be well segregated by using software such as Avizo. As a result,

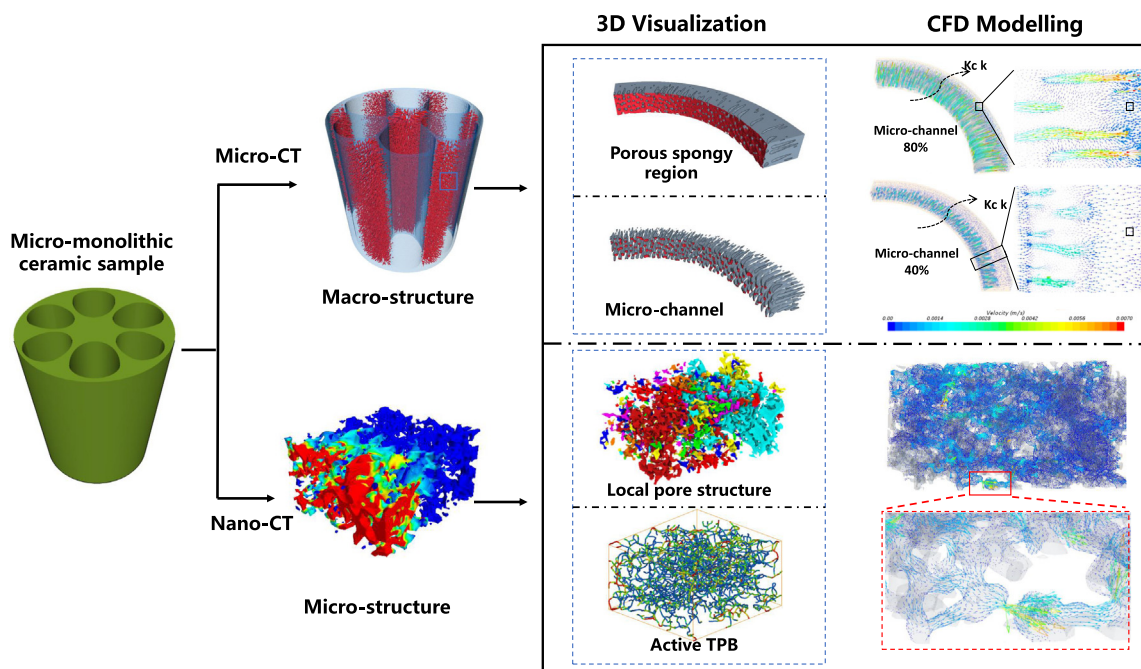


FIGURE 9.13

Examples of multilength scale X-ray computed tomography and reconstruction of micro-structures and nanostructures of ceramic samples. *CFD*, computed fluid dynamics ([Li et al., 2020](#); [Lu et al., 2018](#)).

for the first time, X-CT is used to accurately quantify the micro-channel densities and the cross-sectional dimension along the radial direction. The results can significantly contribute to the knowledge of processing factors that determine the macroscopic and microscopic properties of ceramic membrane fabricated via phase inversion–assisted extrusion. In addition, computed fluid dynamics modelling could help to quantify the influence of micro-channel length (40%–80% of overall cross-sectional thickness) on facilitation of gas transport, the result of which could provide guidance in adjustment of fabrication parameters to achieve the optimum design (Li et al., 2017; Lu et al., 2017a,b,c, 2018).

By combined application of X-CT with multilength scale, Lu et al. (2017a,b,c) carried out intensive studies to understand the effects of mass transport on the rate of reaction and concentration polarization in electrochemical devices, particularly under high operating current density (Lu et al., 2018). It has been reported that the induction of radially grown micro-channels plays a key role in decreasing the tortuosity factor by 50% compared to the conventional electrode design, with the permeability also improved by more than two orders of magnitude. Electrochemical performance simulations incorporating the measured microstructural and mass transport parameters agree quite well with experimental data at all operating temperatures from 700°C to 800°C. The single cell with micro-structured anode displays 70% lower concentration polarization and 60% higher power density (0.98 vs 0.61 W cm⁻²) and a much wider current density window for practical operation than the conventional design (Lu et al., 2018).

9.4 Conclusion

In this chapter, an introduction to micro-structured ceramic membranes and their applications in gas separation and clean energy generation have been presented. The adoption of a phase inversion process in fabrication has resulted in superior control over morphology and significant flexibility in geometric design. The newly developed micro-monolithic ceramic membranes have proved to be a promising solution to the long-existing bottleneck of intrinsic brittleness, increasing the resistance to external bending by several fold and allowing use in a wider array of applications. Gas separation using dense ceramic OPMs demonstrated the distinctive features of high energy efficiencies and theoretically infinite permselectivity. Such OPMs also showed great potential for more complicated chemical reactions, during which natural gas could be transformed into C₂₊ products (e.g., ethylene and ethane), which have higher industrial value. In terms of clean energy generation, OPM functions as the core component in ceramic fuel cells,

which are one of the most promising technologies for sustainable energy generation in the future. Despite reports of some decent performances, most research is still in the early lab stage. However, continued progress can be expected as ceramic membranes for gas separation and energy applications continue to attract more research attention.

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