

## Fabrication of $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta}$ -Based Dual-layer Ceramic Hollow Fibre Membranes for Catalytic Reactions

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### ABSTRACT

In this study, a dual-layer ceramic hollow fibre membrane consisting of two functional layers, i.e. an outer oxygen separation layer ( $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta}$  (BYS)- $\text{L}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSM)) and an inner catalytic substrate layer (BYS-NiO), has been developed using a single-step co-extrusion and co-sintering technique. The key factors in successful fabrication of such membranes and morphology control have been investigated, in which how to match the sintering behaviours of the two layers is critically important. The use of BYS, a great ionic conducting ceramic, is proved to be efficient in promoting oxygen permeation at lower operating temperatures, when compared with previous counterpart,  $((\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.10}(\text{ScSZ})\text{-LSM}$ . This demonstrates its potentials in developing new functional dual-layer ceramic hollow fibre membranes. Moreover, the membranes of this type can be used as a highly compact membrane reactor for catalytic reactions, such as partial oxidation of methane (POM) to syngas and methane combustion, because such a reactor design combines oxygen separation (from ambient air) and methane conversion into a single unit, which significantly reduces the reactor volume due to the extremely high surface area/volume of the hollow fibre configuration.

*Keywords:* Ceramic hollow fibre membrane reactor, oxygen permeation, dual-phase materials, bismuth yttrium oxide (BYS), catalytic reactions

### 1.0 INTRODUCTION

Conversion of methane into more value-added chemical products has widely been investigated in the past few decades, but no feasible cost effective process has yet been developed [1]. Such conversion can be carried out in two ways, either via direct or indirect routes.

Direct conversion provides a path to limited desired products, and in most cases the activation

and conversion of  $\text{CH}_x$  and  $\text{CH}_x\text{O}$  species into the desired products is carried out within a single vessel. The indirect route for methane conversion (e.g. Fischer-Tropsch, Mobil Process and Shell Middle Distillate Synthesis) is a process where methane is converted to other products via synthesis gas ( $\text{CO}$  and  $\text{H}_2$ ).

Fig. 1 illustrates the steps that are involved in the methane conversion via indirect routes, particularly for Fischer-Tropsch process. By employing a novel type of

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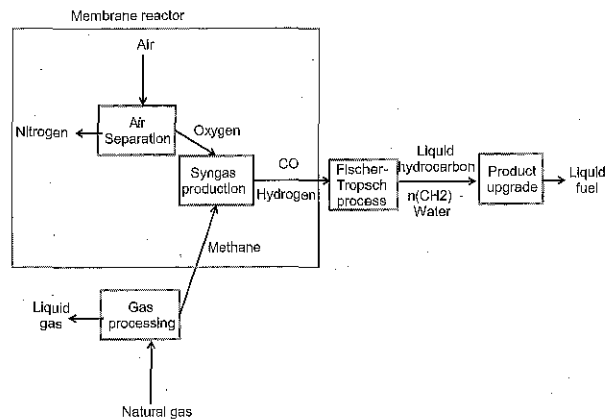


Figure 1 GTL technology for indirect conversion of methane; application of membrane reactor

reactor, such as a membrane reactor, the air separation process and partial oxidation methane process can be integrated into one operating unit, which significantly reduces the capital and production cost. Although there are extensive studies in this area, it is still considered at an elementary level due to a number of challenges, such as the development of reliable membranes for oxygen separation.

In light of this, the main objective of this study is to develop a high performance membrane reactor for methane conversion. In our earlier studies [2-4], it is known that the controlling factor of the membrane reactor design is the oxygen permeation. Therefore, in order to improve the reactor performance, a highly oxygen permeable membrane is favoured. There are two possible routes to enhance the oxygen permeation, which are (1) to develop the membrane reactor using a highly ionic-electronic conductive material and (2) to fabricate a thin oxygen separation layer of oxygen layer onto another porous support.

Over the last decade, extensive researches have been carried out in investigating the potentials of mixed ionic and electronic conducting (MIEC) materials in oxygen separation. From a number of work reported, it is widely accepted that MIEC membranes are in the greatest position as long as the technical challenges on membrane stability and durability can be overcome [5]. Bismuth oxide (BO) is an interesting ceramic due to its high ionic conductivity at intermediate temperatures, which makes it promising to be used for oxygen separation when combined with another electronic conducting ceramic.

The main problem of bismuth oxide (BO) is its stability from 730°C to 825°C [6]. In order to stabilize and further improve the properties of BO, doping approach is utilized. A number of studies have proved that bismuth yttrium samarium (BYS) oxide gives an excellent performance for oxidative coupling of methane (OCM)[7-9]. And in a latest study, a dual phase-material composed of BYS and LSM

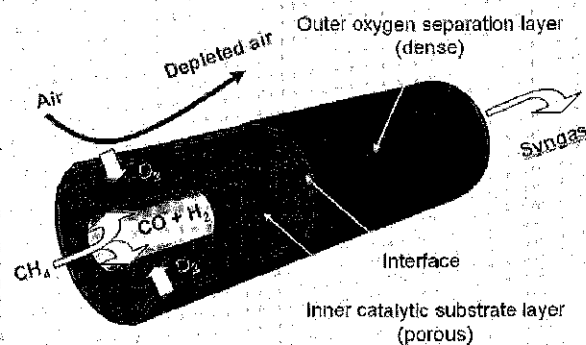


Figure 2 Schematic diagram of DL-CHFMR for POM [11]

[10] has been used to fabricate ceramic hollow fibre membrane, demonstrating the potential of BYs for oxygen separation.

In this study, BYs has been used to develop BYs-LSM/BYS-NiO dual-layer ceramic hollow fibre membranes for catalytic reactions, such as POM (Fig. 2) and methane combustion. For the purpose of comparison, a single-layer BYs-LSM hollow fibre membrane was first developed and its oxygen permeation performance was tested to validate the potential of BYs as the material for membrane reactor. Key factors in fabricating and controlling the structures of BYs-LSM/BYS-NiO dual-layer hollow fibre membranes were investigated, in which how to match the sintering behaviour of the two layers is critically important.

## 2.0 EXPERIMENTAL WORK

### 2.1 Chemicals and Materials

$\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3.8}$  (BYs, 4.44 m<sup>2</sup>/g) was purchased from PraxAir Surface Technologies and calcined at 800 °C before being used. Commercially available  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSM, 5.8 m<sup>2</sup>/g) and NiO were obtained from Fuel Cell Materials and were used as supplied. Dimethyl sulfoxide, (DMSO, VWR), Polyvinylpyrrolidone (PVP-K30, Fluka) and polyethersulfone (PESf, Radal A300, Ameco Performance) were used as a solvent, an additive and a polymer binder for spinning suspension, respectively. Deionized water and tap water were used as a bore liquid and in the coagulation bath during spinning.

### 2.2 Fabrication of BYs-LSM Single-Layer and BYs-LSM/BYS-NiO Dual-Layer Hollow Fibre Membranes

The spinning suspension of the single layer membrane was prepared by dispersing a pre-determined content of ceramic powder into a solution of DMSO/additive. The mixture was left to roll mill (G 91, Gladstone Engineering) for at least 24 hours before adding 10 wt% of PESf. The milling was then continued for 2-3 days to ensure a homogeneous spinning suspension. A similar procedure was used for the preparation of dual-layer spinning suspensions. Table 1 lists the compositions of the spinning suspensions used in this study.

The spinning suspension was first degassed by stirring under vacuum in order to remove the bubbles prior to the spinning. After degassing, the spinning suspension was transferred into a 200 ml stainless steel syringe. The spinning suspension was extruded through a spinneret, passing through an air gap before being immersed into the external coagulant bath. At the same time, the bore fluid was extruded through the central bore of the spinneret, forming the hollow fibre configuration. A tube in orifice spinneret and a triple orifice spinneret were used for the fabrication of single and dual layer hollow fibre membranes, respectively.

The spinning parameters are provided in Table 2. The extrusion rates and the bore fluid flowrate were controlled by a KDS410 and Harvard PHD22/200 Hpsi syringe pumps to ensure the uniformity of the spun fibre. The formed hollow fibre precursors were left

Table 1 Composition of spinning suspensions

	Single layer membrane (wt %)	Dual layer membrane	
		Outer layer (wt %)	Inner layer (wt %)
Ceramic powders:			
BYs	43.69	34.16	41.90
LSM	23.74	27.84	-
Catalyst, NiO	-	-	23.10
Polymer binder, PESf	6.75	6.20	6.50
Additive, PVP 30	2.08	1.00	-
Solvent, DMSO	23.74	30.80	28.50

**Table 2** Spinning parameters for single- and dual- layer hollow fibre membrane

	Single layer	Dual layer
Internal and external coagulant	DI/Tap water	DI/Tap water
Air gap length (cm)	2	25
Single layer extrusion rate	10	-
Inner layer extrusion rate (ml/min)	-	11
Outer layer extrusion rate (ml/min)	-	0.2-5.0
Bore fluid extrusion rate (ml/min)	10-13	10

for 1 hour in the collection tank before being transferred into another tank of fresh de-ionized water, and left overnight to complete the phase inversion and remove the solvent traces.

The hollow fibre precursors were then cut to a specific length and dried at room temperature prior to sintering. In order to transform the fibre precursors to a membranes form, the fibre precursors were sintered using a CARBOLITE furnace. The single- and dual-layer fibres were sintered at 1100°C and 1040°C, respectively and dwelled for 5-12 hours to densify the separation layer.

### 2.3 Characterizations

The sintering behaviour of membrane materials were performed using a dilatometer (NETZCH, DIL 402 C) in static air. Prior to testing, the powder samples were packed into a square-shaped stainless steel mould and compressed using a hydraulic pressure of 1 tonne. A spacer was used between the sample and alumina push rod to avoid contamination.

The phase structure of the membrane materials were investigated using an X'Pert PRO with  $\text{Cu-K}\alpha$  radiation. The XRD scans were carried out at room temperature in 2-theta range from 10° - 80° using a step width of 0.05°. The equipment voltage and current were set at 40 kV and 40 mA.

A JOEL JSM-5610 scanning electron microscope (SEM) was used to observe the morphology of the hollow fibres.

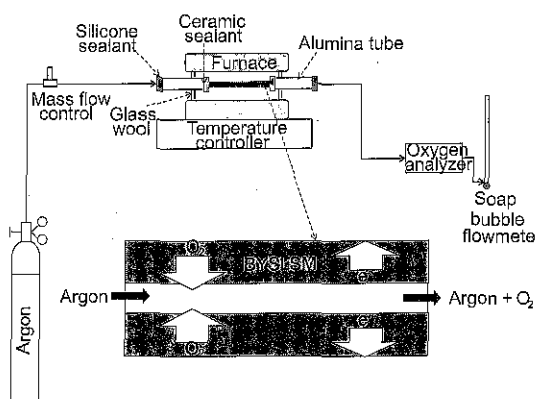
#### 2.3.1 Oxygen Permeation

The measurement of oxygen permeation was carried using the system shown in Fig. 3. Prior to testing, the membrane was sealed between two dense alumina tubes

using ceramic sealant. The furnace was heated up at 5°C/min from room temperature to the target temperature, using a continuous flow of argon in the lumen of the hollow fibre. Ambient air was used as a source of oxygen. The oxygen concentration in the permeate stream was measured using an oxygen analyzer (Model 572 with  $\pm 0.01\%$  resolution, Servomex). Possible gas leakage can be detected by co-monitoring the flow rate of permeates (soap bubble flow meter) and abnormal changes in oxygen concentrations. The oxygen permeation rate is calculated using the following equation:

$$J_{O_2} = \frac{V_1 x_{O_2}}{A_i} \quad (1)$$

where  $J_{O_2}$  is the permeation rate of oxygen ( $\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ ),  $V_1$  is the flowrate of the permeate stream ( $\text{mol}\cdot\text{s}^{-1}$ ),  $x_{O_2}$  is the oxygen concentration obtained from the oxygen analyzer (%) and  $A_i$  is the effective membrane area ( $\text{cm}^2$ ).



**Figure 3** Schematic diagram of oxygen permeation system for single-layer hollow fibre membrane [12]

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Sintering Behavior of BYS-LSM and BYS-NiO

Co-sintering of dual layer hollow fibres is a challenging process especially when it involves more than one type of membrane material. Therefore, sintering curves is a useful tool to understand the sintering behavior of membrane materials. Fig. 4 illustrates sintering curves of the inner and outer-layer membrane materials at two different compositions. The separation layer of the membrane is composed of a dual-phase material (BYS-LSM), while the inner layer consisted of BYS-NiO. BYS is used in both layers to improve the oxygen permeation rate and to match the sintering behavior of the two layers. In order to minimize the membrane defects, the shrinkage of each layer should be as close as possible.

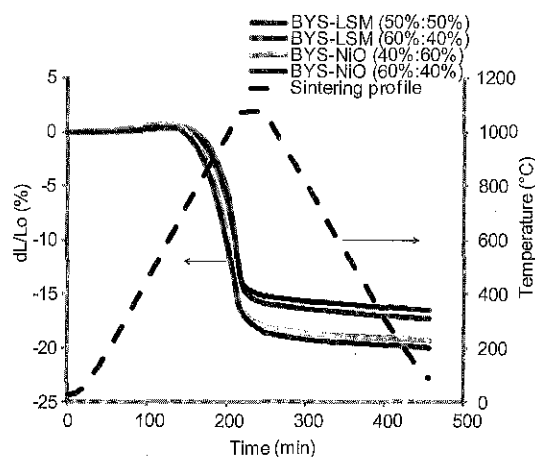


Figure 4 Sintering curves of inner and outer layer samples at different compositions

For the BYS-NiO inner layer, it is observed that the material containing more BYS shows a greater shrinkage, which is opposite to the outer layer. Based on the sintering curves, 40%BYS-60%NiO supposes to be the inner layer material, while the one for the outer layer should be 50% BYS-50 % LSM. However, too much NiO in the inner layer may reduce the mechanical strength, when NiO is reduced into Ni for catalytic reactions, besides possibly more serious coke-deposition. As a result, 60 % BYS-40% NiO was used as the inner layer material for the following membrane fabrication. The final composition of the spinning suspensions

was further adjusted depending on the viscosity of the suspension prepared (Table 1), as an appropriate viscosity of spinning suspension is essential to ensure an easy co-extrusion process and stable fibre formation (avoiding fibre breakage).

#### 3.2 Phase Structure of BYS Powder and Membranes

The X-ray diffraction pattern of the single- and dual-layer membranes that have been crushed into powder is shown in Fig. 5. There are no additional peaks observed after the fibres were sintered at 1040°C and 1100°C, respectively. This suggests good chemical compatibility between the membrane materials. The peak intensity of the single layer membrane was greater than the dual layer one, which is attributed to bigger grain sizes from the higher sintering temperature.

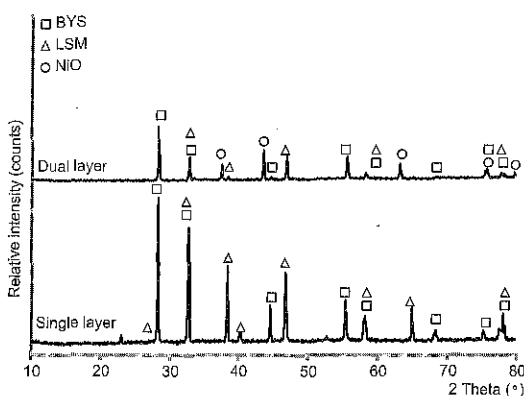


Figure 5 XRD patterns of single- and dual-layer membrane

#### 3.3 Oxygen permeation

Oxygen permeation through the single layer BYS-LSM membrane was measured at different temperatures using argon as the sweep gas. In Fig. 6, it can be seen that the oxygen permeation rate increases, as the operating temperature is increased. This increment is due to higher diffusion rate and faster surface exchange at elevated temperatures. The oxygen permeation at 850°C ( $7.4 \times 10^{-7} \text{ mol.cm}^{-2}.\text{s}^{-1}$ ) is higher than other dual-phase membranes operated at similar conditions, such as BYS-Ag ( $5.8 \times 10^{-7} \text{ mol.cm}^{-2}.\text{s}^{-1}$ )[11], and LSM-YSZ ( $2.10 \times 10^{-7} \text{ mol.cm}^{-2}.\text{s}^{-1}$ )[12]. As such, BYS-LSM is considered as a potential material for dual-layer membrane reactors.

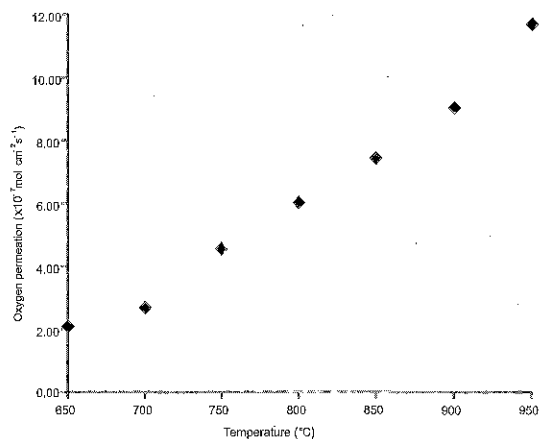


Figure 6 Oxygen permeation of the single layer membrane

### 3.4 Membrane Macrostructure

Fig. 7 shows the cross sections of single-layer fibre precursor and membrane. It can be seen that long finger-like structures emerge from the outer and inner surface of the fibre, and a sponge-like structure, appears at the middle of the fibre. The formation of this sandwiched-like morphology is due to the rapid solvent-non solvent exchange occurs at both inner and outer walls that is in contact with coagulant, resulting in the formation of finger-like structure. A much slower exchange process occurs at the centre of the fibre leads to a denser structure. After the fibre was sintered, it shrunk and became more densified.

The morphologies of the dual-layer membranes are shown Fig. 8. During the co-extrusion process, the outer layer extrusion rate was varied from 0.2 to 5 ml/min, while the one for inner layer was constant, in order to adjust the thickness of the separation layer. The use of a longer air gap during the co-extrusion has resulted in an asymmetric structure, i.e. a sponge-like layer supported on another finger-like layer.

The longer air gap postpones the solvent-non-solvent exchange at the outer surface, which allows further growth of the finger-like voids from the inner surface. It can also be seen that, a higher extrusion rate of the outer layer leads to a thicker separation layer. As the oxygen permeation rate is inversely related to the membrane thickness, when bulk diffusion is the controlling step, a thinner separation layer is preferred for catalytic reactions

### 4.0 CONCLUSIONS

From the single-layer fibre oxygen permeation measurements, it is proved that BYS is a promising material for fabricating functional dual-layer ceramic membranes for catalytic reactions, due to its high oxygen permeation rate at intermediate temperatures. By using the co-extrusion method, the dual-layer hollow fibres have been successfully developed. Further catalytic reaction tests will be carried out to evaluate the potential of BYS as a material for membrane reactor development.

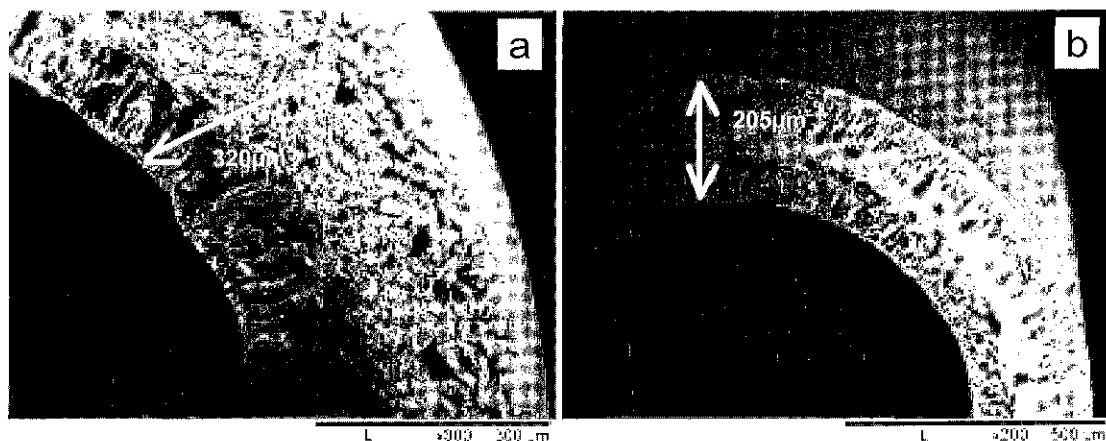


Figure 7 SEM images of single layer fibre: a) precursor and b) sintered membrane

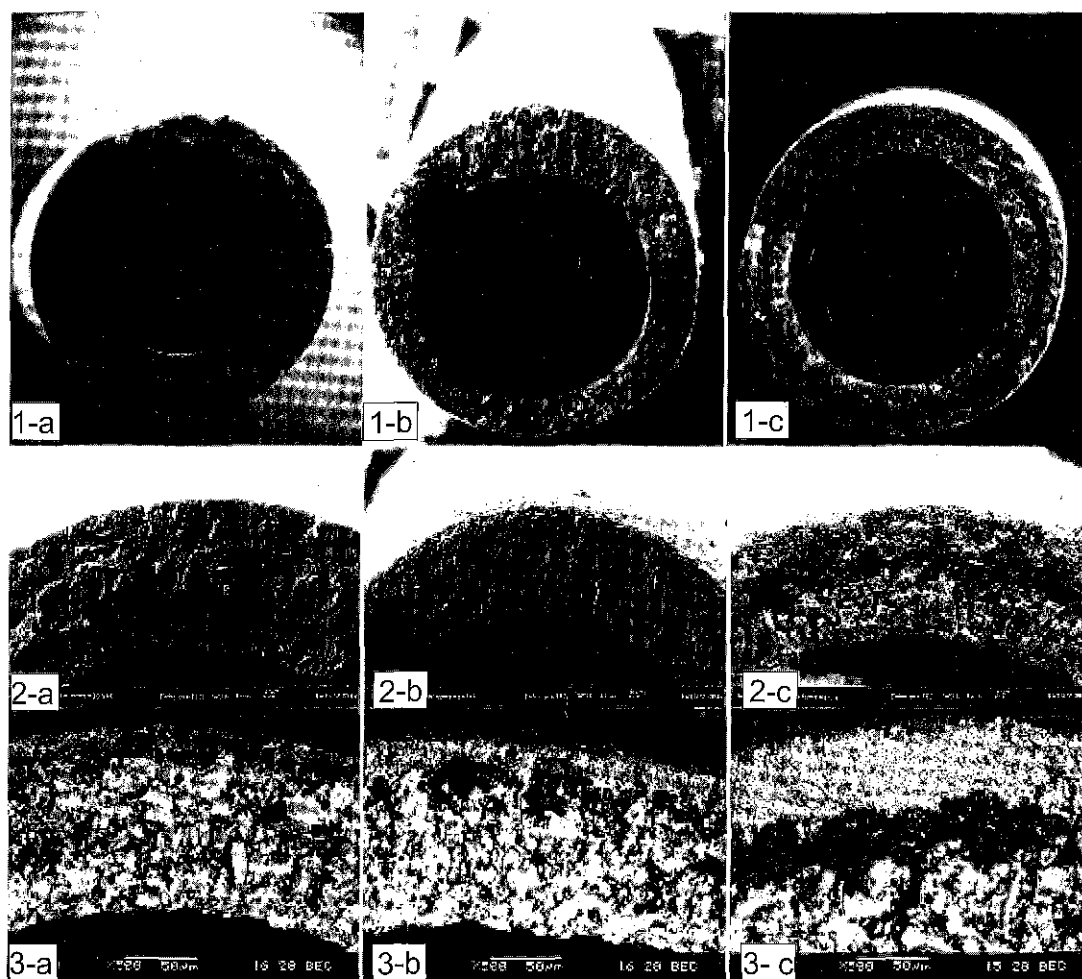


Figure 8 SEM images of dual layer hollow fibre membrane: a) 1.0 ml/min, b) 2.0 ml/min, and c) 5.0 ml/min

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#### REFERENCES

- [1] D. J. Wilhelm, D. R. Simbeck, A. D. Karp, and R. L. Dickenson. 2001. Syngas production for gas-to-liquids applications: technologies, issues and outlook. *Fuel Processing Technology*. 71 : 139-148.
- [2] Z. Wu, B. Wang, and K. Li. 2010. A novel dual-layer ceramic hollow fiber membrane reactor for methane conversion. *J. Membr. Sci.* 352 : 63-70.
- [3] Z. Wu, B. Wang, and K. Li. 2011. Functional LSM-ScSZ/NiO-ScSZ dual-layer hollow fibres for partial oxidation of methane. *International Journal of Hydrogen Energy*. 36 : 5334-5341.
- [4] Z. Wu, A. Thursfield, I. Metcalfe, and K. Li. 2012. Effects of separation layer thickness on oxygen permeation and mechanical strength of DL-HFMR-ScSZ. *Journal of Membrane Science*.
- [5] W. Yang. 2005. Development and Application of Oxygen Permeable Membrane in Selective Oxidation of Light Alkanes. *Topics in Catalysis*. 35 : 155-167.

- [6] D. S. Aidhy. 2010. Effect of ionic polarizability on oxygen diffusion in  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> from atomistic simulation. *Ionics*. 16 : 297.
- [7] Y. Zeng. 2001. F. T. Akin, and Y. S. Lin. 2001. Oxidative coupling of methane on fluorite-structured samarium-yttrium-bismuth oxide. *Applied Catalysis A: General*. 213 : 33-45.
- [8] F. Akin. 2004. Oxygen permeation through oxygen ionic or mixed-conducting ceramic membranes with chemical reactions. *Journal of Membrane Science*. 231 : 133-146.
- [9] Y. Zeng and Y. S. Lin. 2001. Oxidative coupling of methane on improved bismuth oxide membrane reactors. *AIChE Journal*. 47 : 436-444.
- [10] C. Yang, Q. Xu, C. Liu, J. Liu, C. Chen, and W. Liu. 2011. Bi<sub>1.5</sub>Y<sub>0.3</sub>Sm<sub>0.2</sub>O<sub>3</sub>-La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub>- $\delta$  dual-phase composite hollow fiber membrane for oxygen separation. *Materials Letters*. 65 : 3365-3367.
- [11] J. Kim and Y. S. Lin. 2000. Synthesis and oxygen permeation properties of ceramic-metal dual-phase membranes. *Journal of Membrane Science*. 167 : 123-133.
- [12] W. Li, J.-J. Liu, and C.-S. Chen. 2009. Hollow fiber membrane of yttrium-stabilized zirconia and strontium-doped lanthanum manganite dual-phase composite for oxygen separation. *Journal of Membrane Science*. 340 : 266-271.