Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 35 (2009) 1435–1439

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Enhanced oxygen permeation through perovskite hollow fibre membranes by methane activation

Hua Liu [a], Zhaobao Pang [a], Xiaoyao Tan [a,*], Z. Shao [b], J. Sunarso [c], R. Ding [c], S. Liu [c,**]

[a] School of Chemical Engineering, Shandong University of Technology, Zibo 255049, PR China
[b] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, PR China
[c] The ARC Centre of Excellence for Functional Nanomaterials, School of Engineering, The University of Queensland,
Brisbane OLD 4072, Australia

Received 21 April 2008; received in revised form 7 May 2008; accepted 25 July 2008
Available online 5 August 2008

Abstract

Hollow fibre membranes of mixed conducting perovskite $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) were prepared via the combined phase inversion and sintering technique. The fibres were tested for air separation with a home-made reactor under the oxygen partial pressure gradient generated by the air/He streams. Some fibres were in situ activated by introducing methane in the He sweeping gas at high temperatures. The activated membranes with new morphology were created by transforming the inner densified surface layer to a porous structure. Compared to the original membranes, the activated gave appreciable higher oxygen fluxes. At 800 °C, the oxygen fluxes were increased by a factor of 10 after activation was carried out at 1000 °C for 1 h.

Keywords: Hollow fibre; Inorganic membrane; $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$; Perovskite; Oxygen separation

1. Introduction

Oxygen ranks in the top five among the world commercial chemicals. Current tonnage O_2 production by cryogenic process is expensive and energy intensive. New technologies to separate O_2 from air with reduced cost are urgently needed, since most large-scale clean energy technologies require O_2 as feed. For example, if pure oxygen instead of air is used in power plants, the waste gas produced during the combustion process would be pure CO_2 which can be readily and economically captured. Ceramic membranes made from mixed ionic and electronic conducting (MIEC) oxides have received increasing attention because of the possibility to cut O_2 production cost around 35%, thus providing potential to advance these clean energy technologies [1–7]. Among the mixed conducting membranes, perovskite oxides exhibit much higher oxygen permeation fluxes and therefore are actively studied [8–11]. These perovskite membranes can selectively separate oxygen from air at elevated temperatures typically higher than 700 °C, which are promising for use in many industrial processes that require a continuous supply of pure oxygen [12,13]. Over the past several years, extensive efforts have focused on using the MIEC membranes to improve the performance of methane conversion processes, i.e., combining air separation and high-temperature catalytic partial oxidation into a single step. However, these membrane reactor performances are not ideal because of the following two disadvantages: (i) perovskite materials are apt to deteriorate due to the unstable phase structure under reducing, CO_2 containing or low oxygen partial pressure atmospheres and (ii) the disk-shaped membranes with symmetric structure usually suffer high ion transport resistance.

We have recently carried out a project of using catalytic asymmetric ceramic hollow fibre membrane modules for methane conversion [14]. During the permeation process under oxygen gradient provided by air/He, we observed that, the oxygen fluxes through the prepared perovskite hollow fibre membranes have been greatly improved by introducing methane inside the sweep gas for a short activation. This finding seems

---

* Corresponding author. Tel.: +86 533 2313676; fax: +86 533 2313676.
** Corresponding author. Tel.: +61 7 33457914; fax: +61 7 33656074.
E-mail addresses: cestanxy@yahoo.com.cn (X. Tan), s.liu2@uq.edu.au (S. Liu).

0272-8842/$34.00 © 2008 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2008.07.011

contrary to the results of previous work [15–18]. In this brief paper, we described this in situ activation process, the permeation properties of such activated perovskite hollow fibres, and the theoretical explanation. A typical perovskite composition of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) exhibits good oxygen fluxes [8], high mechanical strength and thermal stability, and therefore was chosen as the fibre material for investigation in the present study.

2. Experimental

2.1. Fabrication of ceramic hollow fiber membranes

LSCF hollow fibre membranes were prepared by the phase-inversion/sintering technique. The detailed procedures were described elsewhere [19]. The starting spinning mixture was prepared mixing LSCF powders (surface area of 9.53 m^2/g and $d_{50} = 0.6$ μm, purity > 99.9%) purchased from Praxair Surface Technologies Corporation inside the polymer solution which was composed of polyethersulfone (PESf) [(Radel A-300), Ameco Performance, USA], 1-methyl-2-pyrrolidinone (NMP) [Synthesis Grade, Merck] and polyvinyl pyrrolidone (PVP, K30) [from Fluka, $M_w = 40{,}000$]. A spinneret with the orifice diameter/inner diameter of 3.0/1.2 mm was applied to form the hollow fibre precursors. Deionized water and tap water were used as the internal and external coagulants, respectively. Membrane sintering was carried out at 1300 °C for 5 h to attain the necessary gas-tightness. Microstructure and crystal phases of the hollow fibres were characterized by a scanning electron microscope (FEI Sirion 200, the Netherlands) and X-ray diffractometer (Bruker, D8 Advance), respectively.

2.2. Oxygen permeation through the original and activated fibres

Oxygen permeation properties of the original or activated LSCF hollow fibres were investigated using a high temperature oxygen permeation cell as schematically shown in Fig. 1. Both sides of LSCF hollow fibres were connected in sequence to glass tubes, silicone tubes, and glass tubes by organic bond. A quartz tube (18 mm in diameter and 400 mm in length) was used to house the hollow fibres. The space between the ends of the quartz tube and the glass tube was also sealed by organic bond. Air was fed in the shell side and helium was passed through the fibre lumen to collect the permeate gas. Gas flow rate was controlled by the mass flow controller. The effluent flow rates and compositions were measured respectively by soap bubble flow meter and on-line gas chromatograph (Agilent 6890N) with a 5A column and TCD detector.

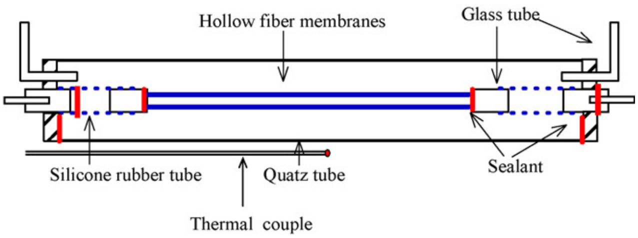

Fig. 1. Configuration of the oxygen permeation cell.

For membrane surface activation, the gas mixture with flow rate of 30 mL/min (50% methane + 50% He) was fed inside the fibre lumen with air flow rate of 200 mL/min in the shell side. Methane activation was carried out at high temperatures (900–1000 °C) for a prescribed time ranged from 1 to 2 h. After activation, methane flow was terminated, leaving He flow continued in the lumen for 20 min to blow away the possible un-reacted methane gas. After that, oxygen permeation fluxes through the activated fibres at different temperatures were measured and analysed similarly as that of the original fibres.

3. Results and discussion

It is well known that polymeric hollow fibre membranes can be formed by spinning a polymer solution inside coagulants like water. Because of the excellent binding capability of some polymers (i.e., polysulfone or polyethersulfone), a large amount of water-insoluble inorganic powders can be mixed inside the polymer solution to form a spinning dope from which the green inorganic hollow fibres can be produced. In this work, LSCF Hollow fibres were made from the mixture of LSCF powder (70.49 wt%) and a polymer solution (PESF: 5.81% + NMP: 23.26% + PVP: 0.44%). Heat treatment was carried out at 1300 °C for 5 h to ensure the formation of the gas-tight membranes. SEM micrographs of a typical LSCF hollow fibre membrane are shown in Fig. 2. The fibre o.d. and i.d. measured from Fig. 1 are 1.7 and 1.1 mm, respectively. The micrograph of Fig. 2b illustrates the asymmetric structure of the prepared LSCF membranes. Near the outer and inner walls of the fibre, short finger-like structures are present; and at the centre of the hollow fibre, sponge-like structures are possessed. Such asymmetric structure was evolved from the green fibre stemmed from the polymer phase inversion process. Fig. 2c and d shows the microstructures of outside and inside surfaces where LSCF particles are closely connected to each other by grain size increasing during sintering process. Gas permeation measurement confirmed the gas-tightness of the prepared membranes. It should be noted that the entire cross-section of the fibre is not fully densified, but no connected porosity is through the membrane. At this stage, we are sure that the gas tightness is resulted from three densified layers with locations on the two surfaces and the centre (marked with white shape) [20]. Fig. 2e shows the surface morphological change after the activation treatment, which will be discussed below.

The experimental results for oxygen permeation through the original and three methane activated hollow fibres at different conditions are shown in Fig. 3. As can be seen from Fig. 3, the oxygen fluxes through all the four fibre samples increase steadily with temperature as a result of the enhancement of oxygen diffusion and surface reaction rates. For example, at helium sweep rate of 25 mL/min, the oxygen fluxes through the original (Fibre-I) and the modified Fibre-II rose from 0.0117 to 0.466 and 0.0637 to 0.725 mL/(min cm^2), respectively, as the temperature was increased from 800 to 1000 °C. Moreover, Fig. 3 also shows that, at the same operating temperature, the

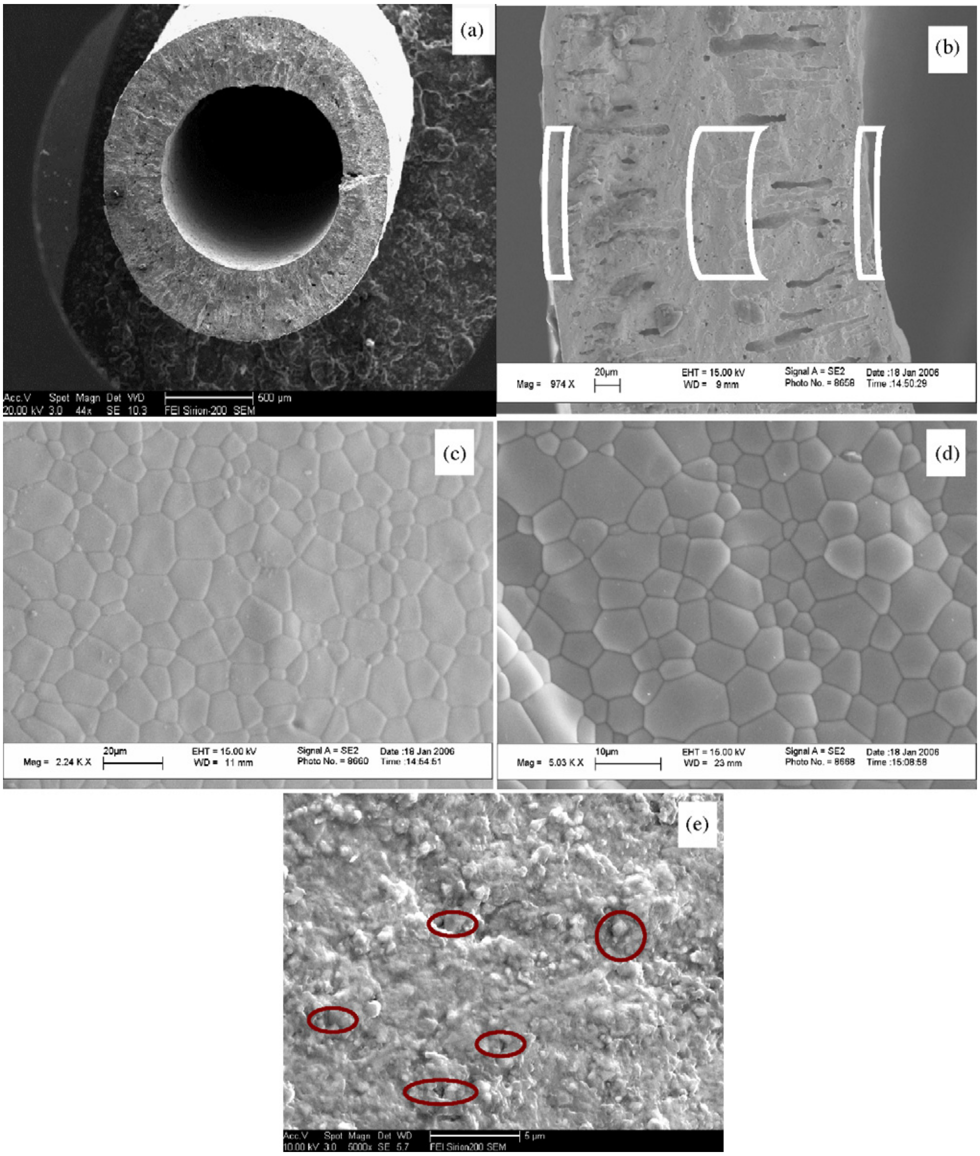

Fig. 2. Typical SEM pictures of the original or activated LSCF hollow fibre membranes (original: lower magnification of cross-section (a); cross-section (b); outer side surface (c); inner side surface (d); after activation at 1000 °C for 2 h: inner side surface (e)). (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

oxygen flux increased with the increase of the helium sweep rate because of lowering the oxygen pressure in the permeate side. For instance, at 1000 °C, increasing the helium flow rate from 10 to 30 mL/min though the Fibre-I and Fibre-II lowered the lumen oxygen partial pressure (average) from 0.11 to 0.054, and 0.142 to 0.083, therefore raised the oxygen fluxes of these two fibres from 0.303 to 0.491, and 0.417 to 0.780 mL/min/cm^2, respectively. Comparing the performance of these samples, it is clear that all the three activated fibres gave better oxygen fluxes than the original fibre, particularly at lower operating temperatures. For example, at 800 °C, the oxygen permeation values have been improved more than 5 times by CH_4 activation at 900 °C for 2 h. Membranes possessing higher fluxes at relatively lower temperatures are more desirable for future commercial oxygen production. Further inspection of the performance of the activated Fibre-II (Fig. 3II) and Fibre-III (Fig. 3III) reveals that the oxygen permeation fluxes have been further improved up to 2 times when the activation temperature was increased from 900 to 1000 °C. A close examination of the permeation results from Fibres-III and IV in Fig. 3 shows that the extension of activation time more than 1 h at 1000 °C is no longer effective to increase the permeation fluxes, indicating that the optimum activation condition should be controlled at 1000 °C for 1 h.

During the activation process, methane in the fibre lumen was oxidized to CO_x or C_2 products (ethane and ethylene) by the permeated O_2. Therefore, perovskite membrane surface would inevitably contact and react with CO or CO_2 to form carbonate or carbonates, some metal oxides and/or metals when the membrane is exposed to air/CO, air/CO_2, air/CH_4 during the permeation experiments. For example, ten Elshof et al. [15] reported that a $SrCO_3$ layer with thickness of 60–80 nm was

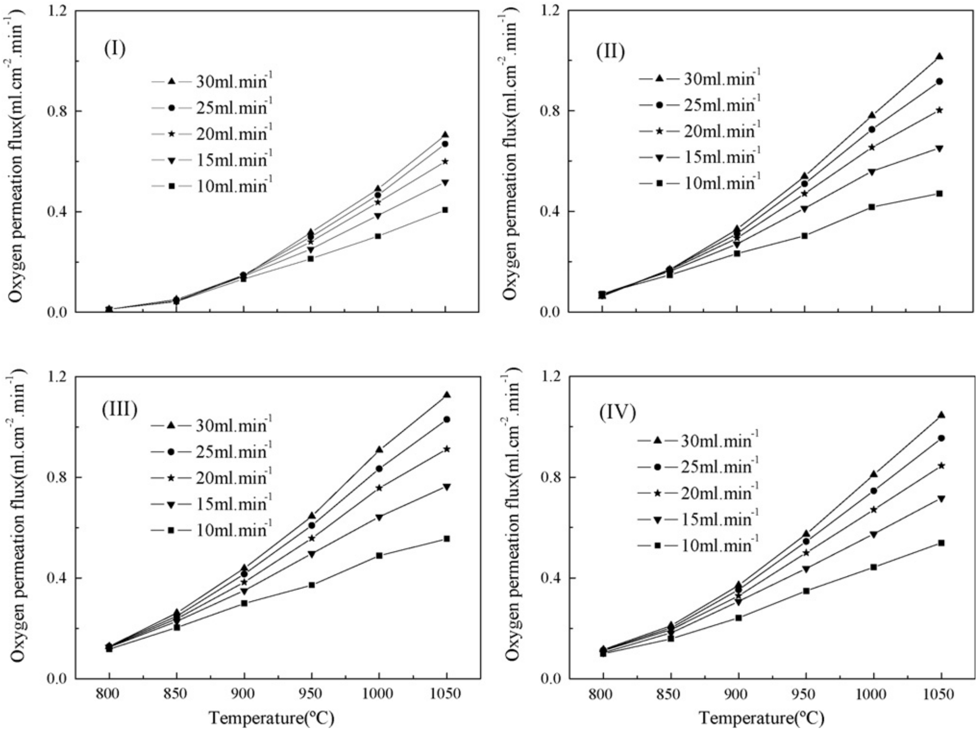

Fig. 3. Effects of operating temperature and helium sweep rates on the oxygen fluxes through the original or methane activated LSCF hollow fibre membranes [original without activation (Fibre-I); methane activation at 900 °C for 2 h (Fibre-II); 1000 °C for 1 h (Fibre-III); and 1000 °C for 2 h (Fibre-IV)].

formed on the membrane surface after the membranes were exposed to the CH_4 containing stream at 1100 K for 3 days. The membrane surface stoichiometry change, the lanthanum and strontium segregation and the formation of small debris crystals when LSCF membranes were applied to methane combustion were also observed by Tan et al. [21]. The formation of new crystal phases has negative effects on the integrity of the membrane due to the mismatch of thermal expansion between these different materials, which caused membrane failure by the problem of peeling off or cracking. Formation of carbonates during the reaction with CO_2 has negative impacts not only on the structural stability, but also on the O_2 permeation flux. Shao et al. reported 30% decrease in oxygen permeation flux for a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane after about 400 h permeation experiment with ambient air/nitrogen at 825 °C [17]. In this work, the finding of better O_2 flux seems contrary to these previous results. However, this phenomenon can be understood by the analysis of the morphological change before and after activation.

As can be seen from Fig. 2e, activation turned the original densified and smooth inner surface into a coarse and porous structure because of the membrane surface deterioration. These pores can be observed with a size of 0.5 μm marked with red rings in Fig. 2e. During subsequent oxygen permeation, the inner surface layer was no longer exerting ionic transport resistance, but providing extra surface area to facilitate the oxygen exchange. Oxygen permeation through a MIEC membrane is jointly affected by the bulk oxygen diffusion and surface exchange kinetics. Compared to the original fibre, the activated fibre has one less densified layer lowering the electrochemical transport resistance, has larger surface area to increase the oxygen exchange rate and therefore has a higher O_2 flux. However, characterizations via EDX and XRD did not find the formation of new phases. One possible reason is that the activation or reaction time is too short and the amount of new phase formation is too small to be detected by the XRD and EDX measurements.

4. Conclusion

Perovskite LSCF hollow fibres were synthesised via a modified phase inversion and sintering technique. The prepared membrane is of the structure of multi-densified layers. Oxygen permeation through the fibres was measured under oxygen concentration gradient of air/He with He as sweep gas in the fibre lumen. Some fibres were in situ activated by introducing methane inside the He for 1 or 2 h at high temperatures ranged from 900 to 1000 °C. The activation changed the inner surface densified layer to a porous structure, decreasing the oxygen ionic transport resistance. The activated fibres gave better oxygen permeation fluxes. Depending on the operating conditions, the activated membranes improved the oxygen fluxes up to 10 times. How to better use the reaction by gas or liquid to optimise the hollow fibre membrane structure for a maximum O_2 flux is still under way.

Acknowledgements

The authors gratefully acknowledge research funding provided by the National Natural Science Foundation of China (NNSFC, nos. 20076025 and 20676073) and financial support of the UQ Early Career Research Grants Scheme (2006001832).

This work was partially supported UQ Early Career Researcher Grants (2006001832). S. Liu also thanks the Australian Research Council for the ARF Fellowship.

References

[1] B. Cales, J.F. Baumard, Oxygen semipermeability and electronic conductivity in calcia-stabilized zirconia, J. Mater. Sci. 17 (1982) 3243.

[2] S.P.S. Badwal, F.T. Ciacchi, Ceramic membrane technologies for oxygen separation, Adv. Mater. 13 (2001) 993.

[3] P.N. Dyer, R.E. Richards, S.L. Russek, D.M. Taylor, Ion transport membrane technology for oxygen separation and syngas production, Solid State Ionics 134 (2000) 21.

[4] Z. Shao, H. Dong, G. Xiong, Y. Gong, W.S. Yang, Performance of a mixed-conducting ceramic membrane reactor with high oxygen permeability for methane conversion, J. Membr. Sci. 183 (2001) 181.

[5] W.Q. Jin, S. Li, P. Huang, N. Xu, J. Shi, Preparation of an asymmetric perovskite-type membrane and its oxygen permeability, J. Membr. Sci. 185 (2001) 237.

[6] H. Wang, C. Tablet, A. Feldhoff, J. Caro, A cobalt-free oxygen-permeable membranes based on the perovskite-type oxide $Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_3$, Adv. Mater. 7 (2005) 1785.

[7] Y. Lin, W. Wang, J. Han, Oxygen permeation through thin mixed-conducting solid oxide membranes, AIChE J. 40 (1994) 786.

[8] Y. Teraoka, H. Zhang, N. Yamazone, Oxygen-sorptive properties of defect perovskite-type $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-a}$, Chem. Lett. (1985) 1367.

[9] S. Liu, G.R. Gavalas, Oxygen selective ceramic hollow fiber membranes, J. Membr. Sci. 246 (2005) 103.

[10] P. Zeng, Z. Chen, W. Zhou, H. Gu, Z. Shao, S. Liu, Re-evaluation of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ perovskite as oxygen semi-permeable membrane, J. Membr. Sci. 291 (2007) 148.

[11] X. Dong, Z. Xu, X. Chang, C. Zhang, W. Jin, Chemical expansion, crystal structural stability, and oxygen permeability of $SrCo_{0.4}Fe_{0.6-x}Al_xO_{3-a}$ oxides, J. Am. Ceram. Soc. 90 (1997) 3923.

[12] H.J.M. Bouwmeester, Dense ceramic membranes for methane conversion, Catal. Today 82 (2003) 141.

[13] X. Tan, K. Li, Oxidative coupling of methane in a perovskite hollow fiber membrane reactor, Ind. Eng. Chem. Res. 45 (2006) 142.

[14] X. Tan, Z. Pang, Gu Zi, S. Liu, Catalytic perovskite hollow fiber membrane reactors for methane oxidative coupling, J. Membr. Sci. 302 (2007) 109.

[15] J.E. ten Elshof, H.J.M. Bouwmeester, H. Verweij, Oxidative coupling of methane in a mixed-conducting perovskite membrane reactor, Appl Catal. A: Gen. 130 (1995) 195.

[16] S. Pei, M.S. Kleefisch, T.P. Kobylinski, C.A.J. Faber, V. Udovich, B.V. Zhang-McCoy, U.B. Dabrowdki, R.L. Mieville, R.B. Poeppel, Failure mechanisms of ceramic membrane reactors in partial oxidation of methane to synthesis gas, Catal. Lett. 30 (1995) 201.

[17] Z. Shao, W. Yang, Y. Cong, H. Dong, J. Tong, G. Xiong, Investigation of the permeation behavior and stability of a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-a}$ oxygen membrane, J. Membr. Sci. 172 (2000) 177.

[18] H. Kruidhof, H.J.M. Bouwmeester, R.H.E. van Doorn, A.J. Burggraaf, Influence of order–disorder transitions on oxygen permeability through selected nonstoichiometric perovskite-type oxides, Solid State Ionics 63–65 (1993) 816.

[19] X. Tan, Y. Liu, K. Li, Preparation of LSCF ceramic hollow-fiber membranes for oxygen production by a phase-inversion/sintering technique, Ind. Eng. Chem. Res. 44 (2005) 61.

[20] H. Liu, X. Tan, Z. Pang, J.C. Diniz da Costa, G. Lu, S. Liu, Novel dual structured mixed conducting ceramic hollow fibre membranes, Sep. Purif. Technol. (2008), in press.

[21] X. Tan, K. Li, A. Thursfield, I.S. Metcalfe, Oxyfuel combustion using a catalytic ceramic membrane reactor, Catal. Today 131 (2008) 292.