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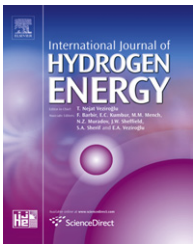

Functional LSM–ScSZ/NiO–ScSZ dual-layer hollow fibres for partial oxidation of methane

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ABSTRACT

In this study, a functional $La_{0.80}Sr_{0.20}MnO_{3-\delta}$ (LSM)–Scandia-Stabilized-Zirconia (ScSZ)/NiO–ScSZ dual-layer hollow fibre has been developed using a single-step co-extrusion and co-sintering process, and has been employed as a dual-layer hollow fibre membrane reactor for partial oxidation of methane. Oxygen permeation rate between 0.49 and 1.82 ml/min and methane conversion between 53.55% and 98.78% have been achieved when operating temperature is elevated from 920 to 1060 °C, together with a significant reduction in coke-deposition. Oxygen permeation through the outer LSM–ScSZ permeation layer (approximately 109.2 μm in thickness) is found to be the controlling step to methane conversion at the operating temperature below 990 °C, above which the excessive oxygen permeation results in formation of CO_2 and H_2O as by-products. The experimental results further suggest that the amount of NiO in the inner NiO–ScSZ layer should be optimised based on the factors such as catalytic activity/stability, porosity and mechanical strength in addition to the sintering behaviour which has to be matched to the outer LSM–ScSZ layer.

1. Introduction

In our recent studies, a single-step co-extrusion and co-sintering process has been employed for fabrication of high quality functional dual-layer ceramic hollow fibre membranes consisting of a thin and defect free outer layer for separation and a highly porous inner support layer with catalytic function for chemical reaction. By proper selection of the membrane materials, i.e. dual-phase materials, multi-functional properties of the fibres for targeted applications have been developed. They has been employed as a compact hollow fibre membrane reactor for methane conversion [1] and used as micro-tubular solid oxide fuel cell (SOFC) [2,3]. Principles of using hollow fibres of this type as a compact membrane reactor for partial oxidation of methane (POM) to syngas, a catalytic reaction of great importance that has been widely studied in respect of catalysis [4,5], membrane separation [6] and simulation [7,8] etc., are schematically shown in Fig. 1, in which oxygen in ambient air permeates exclusively through a fully dense outer separation layer and reacts with methane on a highly porous inner catalytic substrate, forming syngas as the product. This reactor shows advantages including (1) high surface area/volume ratio compared to a conventional flat sheet/tubular counterpart where a catalyst has to be separately packed, (2) less challenges in high temperature sealing and (3) adjustable membrane structures.

Due to the use of dual-phase materials for the functionalized dual-layer fibres, the selection and composition of the materials would greatly affect the co-sintering behaviour as well as performances of the developed membranes. Taking

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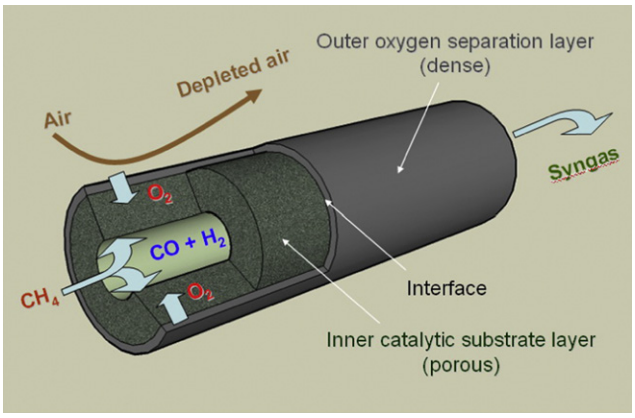

Fig. 1 – Schematic diagram of a dual-layer membrane reactor for methane conversion.

the dual-layer hollow fibre of LSM–ScSZ/NiO–ScSZ to be prepared in this study as an example, as illustrated in Fig. 2, the ratio between LSM, an electronic conducting phase, and ScSZ, an ionic conducting phase, determines oxygen permeation as well as the sintering behavior of the outer layer, while the ratio between NiO and ScSZ in the inner catalytic support layer determines, not only the sintering behavior that has to be matched with the outer layer, but also the catalytic activity, porosity and coking resistance during the actual reactions when NiO is reduced to Ni. Generally, use of more NiO increases porosity of the inner layer after the NiO reduction, which facilitates mass transfer of reactants, but reduces the mechanical strength as well as the coking resistance of the inner layer [9]. Also, for this type of membrane reactor design in which the oxygen separation layer acts as a "distributor" supplying permeated oxygen to the reaction zone, the reactor performance is affected by the "balance" between the oxygen permeation and the catalytic reaction. Insufficient oxygen permeation would limit methane conversion, while excessive supply of oxygen would lead to a deep oxidation and even re-oxidizes Ni to NiO which affects the catalytic activity of the catalyst layer. All these indicate the importance of membrane materials to the development of the dual-phase membranes such as LSM–ScSZ/NiO–ScSZ.

In this study, scandia(10%)-stabilized-zirconia (ScSZ) with better ionic conductivity and coking resistance to methane

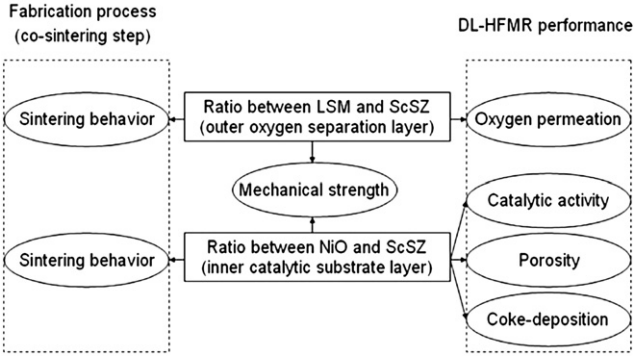

Fig. 2 – Effects of membrane material on fabrication process and reactor performance.

conversion [9,10] has been selected to fabricate an LSM–ScSZ/NiO–ScSZ dual-layer hollow fibre using a single-step co-extrusion and co-sintering process. Adhesion between the two layers at high operating temperatures is discussed. Key factors affecting the membrane fabrication and performances such as co-sintering, oxygen permeation and catalytic activities for methane conversion are investigated.

2. Experimental

2.1. Materials

$La_{0.80}Sr_{0.20}MnO_{3-\delta}$ (LSM, 5.8 m^2/g), NiO (5.2 m^2/g) and scandia (10%)-stabilized-zirconia (ScSZ, 9.4 m^2/g) were used as supplied (NexTech Materials Ltd). Polyethersulfone, (PESf, Radel A-300, Ameco Performance, USA), Dimethyl Sulfoxide (DMSO, Sigma, >99.5%) and Arlacel P135 (Uniqema, UK) were used as polymer binder, solvent and additive, respectively. DI water and tap water were used as the internal and the external coagulants, respectively, when fabricating the dual-layer hollow fibres.

2.2. Determination of membrane material compositions

The outer oxygen permeation layer consisted of 40 vol.% of LSM as an electronic conducting phase and 60 vol.% of ScSZ as an ionic conducting phase, while the inner catalytic substrate was made of a mixture of NiO and ScSZ. Besides catalytic activity/stability, porosity and mechanical strength, the ratio between NiO and ScSZ is the determining factor for the success in co-sintering the dual-layer hollow fibres. As a result, dilatometer (Netzsch, model DIL 402C) was employed to investigate the effects of material composition on the sintering behaviour which has to be matched with the outer counterpart.

2.3. Fabrication of LSM–ScSZ/NiO–ScSZ dual-layer hollow fibres

The preparation of spinning suspensions, the co-extrusion process and the triple-orifice spinneret used to fabricate dual-layer hollow fibre precursors have been described elsewhere [1]. The spinning parameters are listed in Table 1. The formed precursor fibres were cut into the required length, dried and straightened, and finally co-sintered at 1400 °C for 5 h, with heating and cooling rates of 5–10 and 3 °C/min, respectively.

2.4. Characterizations of dual-layer hollow fibres

X-ray diffraction (XRD) was used to investigate the compatibility between membrane materials. Morphology and macrostructure of the developed dual-layer hollow fibres were visually observed using a scanning electron microscope (SEM, JEOL JSM-5610LV, Tokyo, Japan). Sintering behaviours of inner and outer layer materials were investigated using a dilatometer (Netzsch, model DIL 402C) from room temperature to 1400–1450 °C, with a heating rate of 5 °C/min.