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Ionic conducting ceramic–carbonate dual phase hollow fibre membranes for high temperature carbon dioxide separation

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ABSTRACT

In this work, the gas tight ceramic–carbonate dual phase hollow fibre membranes were developed in stages. To this end, oxygen ionic conducting ceramic of yttria stabilized zirconia (YSZ) hollow fibre was firstly prepared and structurally optimised for its application as the porous support to infiltrate the melting carbonate phase at high temperatures. The dual phase hollow fibre membranes were characterised by SEM, XRD, room-temperature gas leakage detection and CO_2 permeation test at temperatures between 550 °C and 950 °C. The maximum CO_2 flux measured reached 0.22 mL cm^{-2} min^{-1} at 950 °C.

1. Introduction

Our human civilisation is facing a severe challenge in this 21st century of how to meet the ever-increasing energy requirement by continuing the usage of fossil fuels but simultaneously to mitigate the impact of climate change due to CO_2 emission. As the combustion of fossil fuels for energy delivery is the largest sector among all CO_2 emission sources, many researchers are developing technologies for CO_2 capture and storage (CCS) from the flue gas emitted from these conventional power plants [1,2]. Among the three CCS schemes (pre or post-combustion and oxyfuel), the post-combustion capture has attracted the most attention as this technology can be easily retrofitted to the existing plants or integrated into new plants with high operational flexibility to be added in stages or operated independently of the power station [3–6]. The traditional chemical method for CO_2 removal from the flue gas is chemical absorption after cooling down, which is very costly due to the treatment of vast amount of flue gas. In this regard, membrane technology is a promising alternative to decrease the capture cost [3]. Since the flue gas is emitted from high temperature sources, it is highly desired to separate CO_2 at a high temperature without cooling to room or even lower temperatures [7,8]. If successful, the concentrated and hot CO_2 can subsequently be used not only for capture and storage, but also as a feedstock directly for value-added chemical synthesis (e.g., methanol) [3,9].

Much effort has been reported on the development of membranes for CO_2 separation. Some polymeric membranes show good perm-selectivity, but their permeances are too low to be of practical interest and none of them are stable at high temperature [10]. A large number of researchers are also devoted to inorganic molecular sieving membranes for CO_2 separation, which offer high permeance and good permselectivity for CO_2 over nitrogen in lower temperatures (<100 °C) [11–14]. The sol–gel-derived microporous zirconia and silica membranes may be used in the intermediate temperature range from 150 to 350 °C for CO_2 separation with a high CO_2 permeance up to $\sim$4.5 mL cm^{-2} min^{-1} under the gas pressure gradient of 1 bar [15–17]. However, all these inorganic membranes with good performance cannot be used for CO_2 separation from the flue gas at temperatures higher than 350 °C.

Recently, some researchers have focused on the dense inorganic dual phase membranes for CO_2 separation [18–20]. Lithium silicate (Li_4SiO_4) membranes on porous alumina supports coated with a molten carbonate mixture (20% K_2CO_3+80% Li_2CO_3) are shown to have a CO_2/N_2 selectivity of 4–6 in the temperature range of 525–625 °C [21]. The CO_2 permeation is completed via the CO_3^{2-} diffusion in carbonates and O^{2-} diffusion in Li_4SiO_4. The reported CO_2 flux for the Li_4SiO_4 membrane at 525 °C was 0.15 mL cm^{-2} min^{-1} [21]. Both of the selectivity and permeance are too low to be considered for practical use. A new class of dual-phase metal-carbonate membrane perm-selective for CO_2 has

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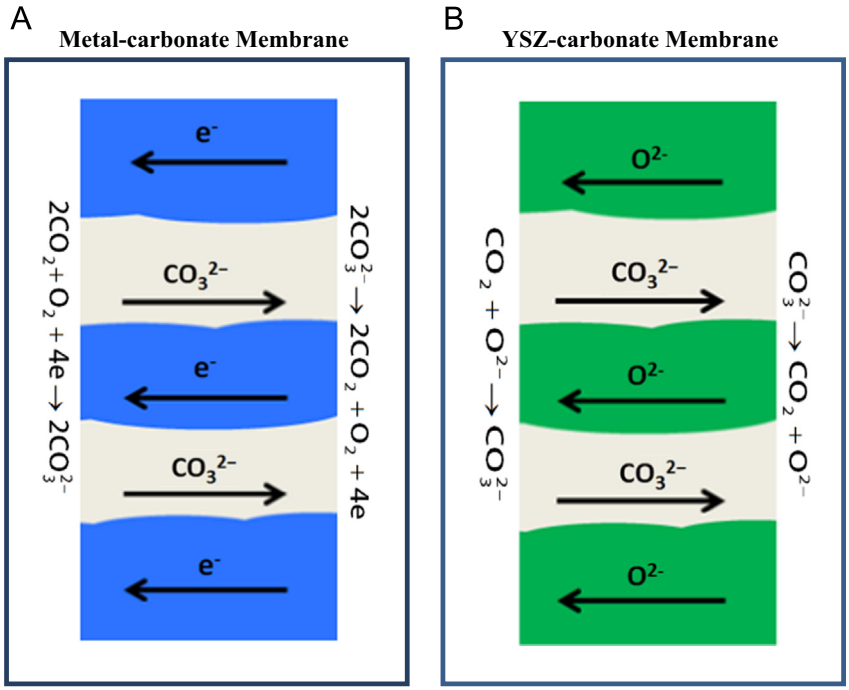

Fig. 1. Schematic illustration showing the difference of surface reactions and bulk diffusions for metal–carbonate membrane (A) or YSZ–carbonate membrane for carbon dioxide separation at high temperatures (Blue colour: metal phase; Green colour: YSZ; Yellow–grey: liquid carbonate). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

been reported by Lin and co-workers [8]. As shown in Fig. 1A, this membrane consists of a porous metal phase and a molten carbonate phase. The metal phase not only serves as a support but also transports electrons. CO_2 separation can be accomplished driven by the CO_2 partial pressure gradient with working principles briefly shown in Fig. 1A. On the upper stream membrane surface (the left side of Fig. 1A), CO_2 combines with electrons and oxygen to form CO_3^{2-}, which is transported through the molten carbonate phase. On the downstream membrane surface (right side of Fig. 1A), the CO_3^{2-} transfers to CO_2 and O_2 via the release of electrons. The electron transports back through the metal phase toward the upstream membrane surface. No external electrodes and connectors are required in this dual-phase membrane simplifying the membrane reactor design. Such dual-phase membranes could give selective permeation of CO_2 and O_2 at high temperatures. Experimental results showed that the stainless steel–molten carbonate dual phase membrane could separate CO_2 between 450 and 650 °C [8]. At 650 °C, the membrane exhibited a CO_2 flux of 0.26 mL cm^{-2} min^{-1} and a CO_2/N_2 perm-selectivity of 16 [8]. There are two major problems for these dual phase membranes. The general metal support like stainless steel is easily oxidised under an O_2-containing atmosphere at high temperatures and therefore the dual phase membrane will gradually lose the function of CO_2 separation. Chemically stable metal materials at high temperatures can be made from silver, platinum or palladium, but they are too expensive [22,23]. Another disadvantage of metal–carbonate membrane is the requirement of O_2 presence in the feed gas and the simultaneous permeation of O_2 lowering the CO_2 selectivity. Despite these shortcomings, this pioneering dual-phase membrane concept still encouraged a lot of research for CO_2 separation at high temperatures. Very recently, researchers have made another progress by the use of more stable ionic conducting ceramics like yttria stabilized zirconia (YSZ), gadolinia doped (GDC) or samaria doped ceria (SDC) [20,24,25]. Compared to the metal–carbonate dual membrane, this ceramic–carbonate dual phase membrane has an improved material stability and a higher CO_2/N_2 selectivity; more importantly, the O_2 presence in the feed gas is no longer required as CO_2 can be transferred to CO_3^{2-} via O^{2-} in the solid phase (lattice oxygen) of YSZ (SDC or GDC) as shown in Fig. 1B. Currently, most of the related research work in this area uses disk-shaped membranes in large thickness. Multiple planar stacks can be designed to scale up the membrane area, but numerous engineering related issues can be envisaged from such flat designs in terms of sealing, connection, pressure resistance etc. Therefore, tubular membranes have been developed to overcome these problems, nevertheless the thick bulk transport layer substantially trade-off their advantages towards practical applications. Also these flat or tubular inorganic membranes have very low surface area/volume ratios ranging from 30 to 250 m^2/m^3 in sharp contrast to more than 1000 m^2/m^3 from the hollow fibre modules [26]. In this regard, membrane geometries in hollow fibre forms seem to find their niche not only in the membrane fundamental studies but also towards scaling up to industrial applications due to the thin gas transport layer, large membrane area per unit volume, and ease of sealing [27–32]. In the past 10 years, ceramic hollow fibre membranes have been largely developed based on the spinning technique via phase inversion to prepare the membrane precursors at room temperature with subsequent sintering at high temperatures to remove all the organics involved [33]. This spinning or extrusion technique has been evolved from the preparation of polymeric hollow fibre membranes and can be tailored to confer the membrane with very thin separating layer [27].

In this work, for the first time, the YSZ–carbonate dual phase hollow fibre membrane was prepared using a combined spinning (or phase inversion), impregnation and sintering method. The hollow fire membrane was tested at high temperature for CO_2 separation from a CO_2–N_2 mixture.

2. Experimental section

2.1. Porous YSZ hollow fibre preparation

The porous YSZ was prepared by the combined phase inversion and sintering method. The YSZ powder was added to a mixture of