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Surface activation of asymmetric $CaTi_{1-x}Fe_xO_{3-\delta}$ tubular membranes for oxygen separation

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ABSTRACT

Tubular asymmetric mixed ionic-electronic conducting $CaTi_{0.9}Fe_{0.1}O_{3-\delta}$ (CTF) membranes can be used for oxygen separation from air. However, the oxygen permeation flux through thin CTF supported membranes may be limited by surface oxygen exchange kinetics and gas diffusion limitation in the porous support. To overcome surface exchange limitation, the membranes can be coated with an activation layer, which can either be a porous layer of the membrane material itself to increase the active surface area, or a porous layer of a material exhibiting superior oxygen exchange properties. In this study, asymmetric tubular CTF membranes were prepared by plastic extrusion and dip-coating. The membranes were further coated by spray-coating with both types of activation layers. $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ (LSC) or $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) were selected based on similar thermal expansion and high mixed ion and electron conductivity. We report here on the effects of spray-coating parameters and annealing treatment on both the adhesion and the porosity of the spray-coated layers. In addition, we discuss results of oxygen flux and permeability in the temperature range 750–1000 °C in relation with potential limitations from surface exchanges and gas diffusion in the porous tubular supports.

1. Introduction

Mixed ionic electronic conducting (MIEC) membranes have received large attention during the last decade due to their potential for separating oxygen from air for instance, in oxy-combustion of coal to facilitate CO_2 capture. When coal is combusted with pure oxygen instead of air, a flue gas consisting mainly of H_2O and CO_2 is produced, from which CO_2 is easily captured for subsequent storage [1–3]. High flux MIEC membranes are mostly made of materials crystallising in a perovskite structure ABO_3, and operate at temperatures typically ranging between 700 and 1000 °C in large oxygen partial pressure gradient [4,5]. These high operating temperatures impose strong demands on the membranes. As example, state-of-the-art $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) membrane exhibits high oxygen flux, but suffers from low stability in reducing environment as well as kinetic demixing and decomposition in chemical gradient [6]. To overcome these challenges, membrane materials may be chosen so as to achieve a reasonable compromise between high flux and stability (mechanical, thermal and chemical) in long term operation. Compared to BSCF, Co-free membranes such as $CaTi_{1-x}Fe_xO_{3-\delta}$ are more stable under reducing conditions and in large oxygen partial pressure gradients. In addition, these membranes exhibit steady performance when operated in CO_2 containing atmospheres. This improved stability allows for a more efficient integration of the membrane module in the oxyfuel power plant, in contrast to stand-alone air separation units [7]. However, the oxygen flux of CTF membranes is several times lower than BSCF membranes when comparing membranes with similar thickness [8]. This imposes the use of thinner CTF membranes to achieve higher flux, provided that the oxygen flux through the membrane is controlled by bulk diffusion. As thin membranes are usually coated on porous supports to ensure required mechanical strength of the assembly, deviation from the Wagner equation may already be observed due to gas diffusion limitation in the porous support. In addition, if the thickness of the membrane is thinner than a critical thickness L_c, the oxygen flux will be strongly limited by surface exchange kinetics [9,10]. The oxygen flux may be improved by increasing kinetics of gas exchange at the membrane surface. This can be achieved e.g. by enlarging the external surface area of the membrane by coating the membrane with a porous layer of the same material. This has been studied for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) membranes.

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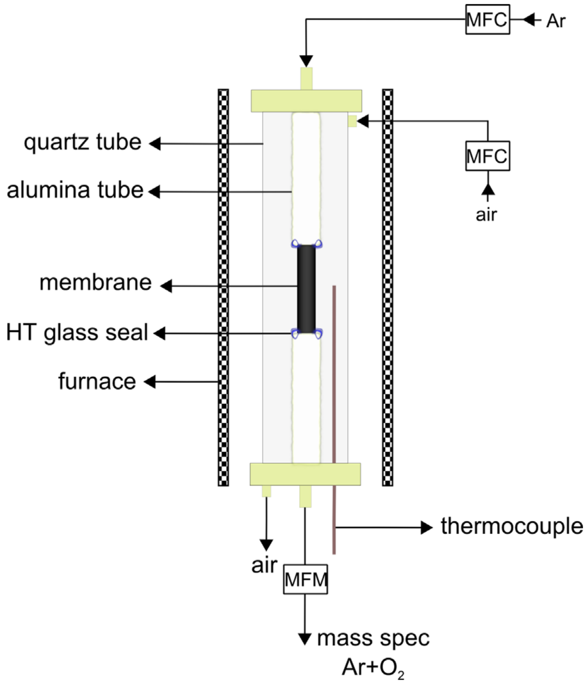

Fig. 1. Scheme of the oxygen permeation measurement setup for tubular membranes.

Tan et al. coated LSCF hollow fibre with a porous 20 μm thick LSCF layer, which resulted in a 9-times increased oxygen flux compared to the uncoated membrane at 800 °C [11]. The effect of surface loading of 11 mg cm^{-2} of a porous $La_{0.3}Sr_{0.7}CoO_{3-\delta}$ layer coated on $La_{0.3}Sr_{0.7}CoO_{3-\delta}$ disk membrane was studied by Kharton et al. They found an increased permeation flux of up to 50% [12]. Another possibility to improve the surface oxygen exchange kinetics is to apply a catalytic layer of a different material with higher surface exchange coefficient. This can be a metal, such as Ag, Pt and Pd, though this may give a significant increase in the cost of the membranes and potentially also long term stability issues related to agglomeration or evaporation of catalysts in operation. Examples of coatings with metals are silver coating with a surface loading of about 5 mg cm^{-2} on LSCF hollow fibre membranes, which leads to an increase of about 17% of the flux at 800 °C [11]. A silver coating had also shown a positive effect on the flux of $La_{0.3}Sr_{0.7}CoO_{3-\delta}$ membranes when operating the coated membrane above 700 °C [12]. An improvement of 86% of the flux was obtained by applying Ag catalyst on $CaTi_{0.8}Fe_{0.2}O_{3-\delta}$ disk membrane [13]. 3 mg cm^{-2} Pt coating on LSCF hollow fibre membranes enhanced the oxygen flux by a factor of 4 at the lower temperatures [14]. The effect of Pd coating on LSCF hollow fibre membranes yielded an improvement of 350% of the flux compared to uncoated membranes [15].

Another MIEC material with higher surface exchange coefficient may be used, though the selection of chemically compatible material with the membrane is not straightforward. Pan et al. coated LSCF hollow fibre membranes with several perovskite related materials, such as $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCFe), $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$ (SCSc) and BSCF [16]. The best enhancement was obtained with SCSc coating. Teraoka et al. studied the effect of $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ coating on LSCF disk membranes, which resulted in a small increase in the oxygen flux [17]. Moreover, Lee et al. measured oxygen flux for $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_{3-\delta}$ membranes 2–6 times higher than pristine membrane by applying a $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ layer [18,19].

In this study, we investigate possibilities for enhancing the oxygen flux of $CaTi_{0.9}Fe_{0.1}O_{3-\delta}$ (CTF) membranes by addressing surface kinetics limitations of CTF supported membranes. The membranes are produced as dense films of 40–70 μm thickness coated on porous tubular supports. The flux of the membrane may be limited by both surface kinetics and eventually gas diffusion limitations in the support. The tubular asymmetric CTF membranes were spray-coated with porous CTF, LSC and LSCF activation layers. This scalable deposition technique has been demonstrated by Lee et al. to produce palladium film on a porous yttria stabilized zirconia substrate, while Liu et al. prepared an asymmetric $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ (SCFZ) tubular membrane by depositing a thin SCFZ layer on a porous SCFZ substrate [20,21]. Spray-coating allows applying dense or porous activation layers with a controlled thickness on flat and tubular substrates. The produced activation layers were characterised for their microstructure, thickness and porosity as function of the processing parameters. Furthermore, the effect of the coatings on the oxygen flux and permeability was studied in an attempt to define preferred catalytic material.

2. Experimental

2.1. Preparation and characterisation of asymmetric tubular CTF membranes

CTF porous supports were prepared by plastic extrusion using a 40 tons Loomis ram extruder equipped with a 70 cm diameter and 1 m length barrel. The extrusion feedstock was prepared by mixing CTF powder (Saint-Gobain CREE, France) with a commercially available dispersant (Darvan C, RT Vanderbilt), a binder system developed at SINTEF and a lubricant. Water was used as solvent. Pyrolyzable pore formers were used to increase the open porosity of the supports after sintering. The green tubes were dried in a controlled atmosphere (adjusted temperature and moisture content) to avoid uneven shrinkage upon drying and subsequent deformation during sintering. The dried tubes were cut as 15 cm pieces and pre-annealed in air at 1000 °C for burnout of organic additives. The pre-annealed tubes were dip-coated in an organic based suspension prepared by dispersing CTF powder in isopropanol with a dispersant and a binder. The suspension was homogenised for several hours in a planetary miller at 300 rpm using zirconia balls and jar. Several dipping steps were carried out with a withdrawal speed of 3 cm min^{-1} to vary the thickness of the membranes. The coated tubes were sintered in air at 1400 °C. Scanning electron microscopy (SEM) analysis and bubble leak tests at room temperature were carried out to verify the quality of the produced membranes.

2.2. Surface modification of CTF membranes

Slurries of $CaTi_{0.9}Fe_{0.1}O_{3-\delta}$, $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ materials were prepared. Each slurry was prepared by first mixing ethyl cellulose binder (ACROS Organics) with ethanol (96%, Merck) until a clear solution was obtained. Then, polyvinyl pyrrolidone (Janssen Chimika) was added. Afterwards, CTF powder (Saint-Gobain CREE) or LSC powder (Marion Technology) or LSCF powder (Treibacher) was added to the solution. The slurry was stirred until a homogeneous mixture was obtained. Each slurry contained about 20–30 wt% ceramic loading. Prior to its use, each slurry was kept under agitation for at least 24 h.

The slurries were applied on rotating asymmetric tubular CTF membranes using a spray gun with pressurised air. The spray gun to membrane distance, the amount of sprayed fluid and pressurised air, the rotation speed and the linear speed of the spray gun were all optimised in order to obtain a uniform coating on the membranes. This was obtained by setting the spray gun to membrane distance at 10 cm and by using a spray flow rate of 0.3 ml min^{-1}. Different amount of